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A STUDY OF THE TEMPERATURE COEFFICIENTS OF CONDUCTIVITY IN AQUEOUS SOLUTIONS AND ON THE EFFECT OF TEMPERATURE ON DISSOCIATION.

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INTRODUCTION.

It is now generally recognized that ions are the chief agents which bring about chemical action. The chemical activity of solutions is, then, a function of the dissociation of the dissolved substances. Since conductivity is a measure of dissociation, there is, therefore, a close relation between the conductivity of solutions and their chemical activity. The conductivities of a large number of substances in aqueous solutions have been determined at 18° and 25°, while at other temperatures not very much work has been done. It is well known, however, that the conductivity of solutions is greatly affected by temperature. Consequently, a study of the exact effect of temperature on the conductivity of aqueous solutions

and on their dissociation, is of considerable importance, especially for those temperatures and dilutions more frequently employed in the determination of conductivity. The temperatures in question range from 0° to 35° and the dilutions from N/2 to N/1024.

Historical Review.

Quite a number of investigators have studied the effect of temperature on conductivity and some interesting results have been obtained, not only at intermediate temperatures, but at those below 0° and above 100°. It was very early observed that conductivity is affected by temperature. Ohm[1] noticed this fact in 1844 and two years later Hankel[2] made the same observation. The problem was not seriously considered, however, until some years afterwards, when Grotrian[3] took it up. He determined the conductivity of a few dilutions of sulphuric and hydrochloric acids, at various temperatures, and showed that the effect of temperature on conductivity, in the case of sulphuric acid, could be represented by an equation of the form

$$L = L_0 (1 + \alpha t + \beta t^2),$$

and in the case of hydrochloric acid the temperature effect could be represented by the formula

$$L = L_0 (1 + \alpha t).$$

In each of these formulas L represents the molecular conductivity, t is the temperature in question, and α and β are constants.

Kohlrausch and Grotrian,[4] a year later, studied the influence of temperature on conductivity. They worked out the temperature coefficients of a few acids and salts, and suggested that the effect of temperature on conductivity could be best represented by the formula which Grotrian had deduced for sulphuric acid.

Other investigators have determined temperature coefficients

[1] Pogg. Ann., 63, 403 (1844).
[2] *Ibid.*, 69, 255 (1846)
[3] *Ibid.*, 151, 378 (1874).
[4] *Ibid.*, 154, 224 (1875).

of conductivity but, in many cases, they studied only a few compounds at various dilutions.

Krannhals[1] determined the conductivity of hydrochloric acid and a few inorganic salts, over a range of temperature extending from 18° to 100°. He found, as others before him had done, that conductivity increases with rise in temperature and with increase in dilution. He concluded from his results that temperature has no effect on dissociation. Rudolphi[2] made some conductivity measurements between 25° and 100°. His results also showed that temperature has practically no effect on dissociation. Jahn[3] determined the conductivity of a number of fatty acids between 10° aad 50°. He measured dilutions only as high as N/128, consequently, his dissociation values could not be very accurate. Others who have made conductivity measurements at different temperatures and calculated temperature coefficients, are Bouty,[4] Long[5] and Freund.[6]

Arrhenius,[7] in 1887, showed the connection between the lowering of the freezing-point of a solvent by an electrolyte and the conductivity of the electrolyte. In most of the earlier experiments, however, the values obtained for the amount of dissociation at 0°, by the freezing-point method, were generally a little higher than those obtained by the conductivity method at 18° and 25°. This would indicate that there is a small negative temperature coefficient of dissociation. Two years later Arrhenius[8] studied this problem. He worked out the temperature coefficients of conductivity of a number of salts, at various temperatures, ranging from 18° to 52°. His results showed that temperature has little or no effect on dissociation.

Déguisne[9] studied the effect of temperature on conductivity in very dilute, or completely dissociated solutions of strong

[1] Z. physik. Chem., **5**, 250 (1890).
[2] *Ibid.*, **17**, 385 (1895).
[3] *Ibid.*, **16**, 72 (1895).
[4] Ann. Chim. Phys., [6], **3**, 498 (1884).
[5] Wied. Ann., **11**, 37 (1880).
[6] *Ibid.*, **7**, 47 (1879).
[7] Z. physik. Chem., **1**, 631 (1887).
[8] *Ibid.*, **4**, 96 (1889).
[9] Dissertation, Strassburg (1895).

electrolytes. He worked at various temperatures from 0° to 34° and expressed the influence of temperature, t, on the conductivity, K, starting from 18° as a mean temperature, in the form of the following equation :

$$Kt = K_{18}\,(1 + \alpha(t-18) + \beta(t-18)^2).$$

R. W. Wood[1] measured the conductivity of several electrolytes in dilute solutions, at 0°. He calculated the dissociation at 0° and compared his values with those obtained by Kohlrausch at 18°. He found, as others had done before him, that, in dilute solutions, temperature has practically no effect on dissociation.

Schaller[2] made conductivity measurements of several electrolytes in dilute solutions, at various temperatures between 25° and 100°. In order to avoid the action of water on glass at high temperatures, he employed a platinum vessel, but it was found that in the case of acids and neutral salts, vessels made of Jena glass might be used. The conductivity was found to increase with rise in temperature, but at a diminishing rate. The dissociation was found to decrease with rise in temperature. Schaller, however, did not work at temperatures as low as 0°, so that the exact effect of temperature on dissociation, for temperatures ranging from 0° to 25°, was still an unsettled question.

Whetham[3] carried out a very careful piece of conductivity work at 0°, for the purpose of comparing the dissociation values thus obtained, with those worked out by the freezing-point method a little below 0° and also with the values obtained by Kohlrausch at 18°, using the conductivity method. He worked with several electrolytes and found that dissociation decreased very slightly with rise in temperature.

Douglas[4] studied the effect of temperature on the conductivity of a number of electrolytes. He worked with several acids, bases and salts at various temperatures, ranging from

[1] Phil. Mag., 41, 117 (1896).
[2] Z. physik. Chem., 25, 497 (1898).
[3] Phil. Trans., 194, 321 (1900).
[4] This Journal, 26, 428 (1901).

0°–35°. His results indicate that temperature has practically no effect on dissociation.

As we have seen, Whetham's results obtained the year before indicated that there was a very slight decrease in dissociation with rise in temperature. Thus the problem as to the exact effect of temperature on dissociation, over a range of temperature extending, say, from 0°–35°, was still an unsettled one. Some important investigations have been carried out at temperatures below 0° and above 35°, and some interesting results have been obtained.

Kohlrausch[1] pointed out that it was probable that the conductivities of all aqueous solutions approach, with decreasing temperature, a zero value at about the same temperature, which is —38°.5, and that the cause of this phenomenon is to be sought for in the disappearance of the fluidity of water at this temperature. In a later paper, Kohlrausch[2] showed that, if the conductivity curves of a number of electrolytes were extrapolated below 0°, in accordance with Déguisne's formula, they would all approach a zero value of conductivity at about —38°.5. He also pointed out the fact that, if the curves showing the relations between fluidity and temperature were extrapolated, they would also cut the zero axis at about the same point. That is, conductivity and fluidity disappear at the same point. Of course, wide extrapolation is necessary, and this fact must be taken into account. What is more significant, the conductivity curve for certain salts, notably sodium valerate, is almost identical with the fluidity curve, and further, the temperature coefficient of ionic mobility, in the case of slow moving ions, is almost the same as that of fluidity. In order to explain these facts and avoid the assumption that ionic motion is independent of the motion of the solvent, Kohlrausch proposed the hypothesis that about every ion there moves an atmosphere of the solvent, the dimensions of which are determined by the individual characteristics of the ion. The direct action between the ion and the solvent diminishes as the atmosphere becomes of greater dimensions. This hy-

[1] Sitzun. Berlin, 1028 (1901).
[2] P. Roy. Soc., 71, 338 (1903).

pothesis accounts for the apparent disappearance of fluidity and conductivity at the same temperature. The idea of ionic hydration was not entirely original with Kohlrausch. Ciamician,[1] some years before, had suggested that around every ion there is a shell of water. He also attempted, by diffusion methods, to measure the amount of this hydration.

Kunz,[2] at the suggestion of Kohlrausch, made some conductivity measurements on sulphuric acid at various temperatures, ranging from 0° to —70°. He worked with several solutions of various concentrations, from 19.1 to 63.76 per cent. His conductivity curves, representing conductivity as a function of temperature, do not meet the temperature axis at —38°.5, as Kohlrausch had predicted. Instead of the curves converging at one point, they approach the abscissa more and more slowly as the temperature falls. Kunz adopted the view that electrical resistance is due to friction. In a later article, Kunz[3] stated that he had obtained similar results with calcium chloride and sodium hydroxide. These results would seem to indicate that the hypothesis of Kohlrausch could not easily be demonstrated experimentally.

In an interesting article, W. R. Bousfield and T. M. Lowry[4] point out the effect of temperature on conductivity over a wide range of temperature. They show that conductivity-temperature curves cannot be represented by a linear or parabolic formula, as Kohlrausch has suggested. At high and low temperatures, no general formula will account for the facts. The conductivity-temperature curves, when plotted for a long range of temperature, are all inflected curves which contain a maximum point.

At low temperatures, the effect of temperature on conductivity is determined mainly by the changing mobility of the ions. At higher temperatures, the change in dissociation becomes a dominant factor and, just as the increasing viscosity of the solution leads at lower temperatures to a lower conductivity zero, at which the viscosity of the liquid would alto-

[1] Z. physik. Chem., 6, 403 (1890).
[2] Compt. rend., 135, 788 (1902).
[3] Z. physik. Chem., 42, 591 (1903).
[4] P. Roy. Soc., 81, 467 (1902).

gether prevent ionic mobility, so at higher temperatures an upper limit may exist, at which the conductivity would again become zero, owing to the complete disappearance of dissociation. The different behavior of acids and salts, which is unimportant in the case of the lower conductivity zero, becomes a vital factor in discussing the possible existence of an upper conductivity zero.

Armstrong[1] called attention to the fact that, while the majority of salts are conductors, *per se*, the acids are, in the pure state, dielectrics and only become electrolytes by interaction with a dissociating solvent. In virtue of their inherent power of self-ionization, the salts may, therefore, exhibit some conducting power, independent of that due to the dissociating properties of the solvent, while it is to be expected that the acids would cease to be electrolytes if the solvent, by reason of increasing temperature, should lose its power of dissociation. For this reason, evidence of the existence of an upper conductivity zero is to be looked for, in solutions of substances which, like the acids, are incapable of self-ionization.

Arrhenius[2] pointed out the effect of decreasing dissociation with rise in temperature, in the case of phosphoric and hypophosphoric acids, which exhibit maxima of conductivity at 54° and 75°, respectively. Sach[3] also observed this phenomenon in the case of aqueous solutions of copper sulphate. In the majority of cases the maximum of conductivity lies above the boiling-point, and experimental work is rendered very difficult, owing to the ready solubility of glass at high temperatures.

Miss Maltby[4] found that, on heating up to 237°, the conductivity of an aqueous solution of potassium chloride reached a maximum and decreased as the temperature rose. Hagenbach[5] observed a maximum in the conductivity of a 0.01 N solution of potassium chloride. In these experiments the conductivity cells were of glass, consequently the results were not very accurate. Noyes and Coolidge[6] studied the effect of tem-

[1] P. Roy. Soc., **40**, 268 (1886).
[2] Z. physik. Chem., **4**, 96 (1889).
[3] Wied. Ann., **43**, 212 (1891).
[4] Z. physik. Chem., **18**, 155 (1895).
[5] Ann. d. Phys., **3**, 276 (1901).
[6] Z. physik. Chem., **46**, 323 (1904). J. Am. Chem. Soc., **262**, 134 (1904).

perature on the conductivity of aqueous solutions of sodium and potassium chlorides. They worked at various temperatures ranging from 140°–306°. At 280° the conductivity curves of both chlorides for 0.1 N solutions reach a maximum and then fall. They proved, in the case of a 0.5 N solution of the salts, that these maxima in the curves would probably be much more pronounced. Their results show that, at the higher temperatures, there is a marked decrease in dissociation. In their work they used a steel bomb lined with platinum, which would eliminate any error arising from the solubility of glass.

There is more evidence available for the existence of conductivity-temperature curves containing maxima and perhaps an upper conductivity zero, as was pointed out by Messrs. Bousfield and Lowry, in the case of non-aqueous solvents. Franklin and Kraus[1] found that, at high temperatures, the conductivity of solutions in liquid ammonia decreases with rise in temperature. Miss Maltby[2] has shown that, even at atmospheric temperatures, the conductivity of an ethereal solution of hydrochloric acid decreases as the temperature rises. Cattaneos[3] obtained negative temperature coefficients in solutions in ether, alcohol and glycerol. Hagenbach[4] obtained maxima in the conductivity-temperature curves at about 120°, in solutions of several salts in liquid sulphur dioxide. Walden and Centnerzwer[5] determined the conductivity of hydrochloric acid and a number of organic compounds, dissolved in sulphur dioxide. The results with hydrochloric acid are especially interesting, because it is known to be of itself a non-electrolyte, and to possess no power of undergoing dissociation, unless brought in contact with a dissociating medium. At the critical temperature of the solvent, the conductivity decreased to a zero value, which is, therefore, identical with the upper conductivity zero of the solution. Kraus[6] investigated solutions of various electrolytes dissolved in methyl and ethyl alcohols.

[1] THIS JOURNAL, 24, 83 (1900).
[2] Z. physik. Chem., 18, 133 (1895).
[3] Rend. Lincei, [5], 2, 1, 295 (1893); *Ibid.*, [5], 2, 2, 112 (1893).
[4] Ann. d. Phys., [5], 2, 276 (1901).
[5] Z. physik. Chem., 39, 549 (1902).
[6] Phys. Rev., 18, 40 (1904).

He studied the conductivity up to, through and beyond the critical temperature of the solvents, and showed that the conductivity-temperature curve passes through a maximum with rise in temperature. The maximum in the case of solutions in methyl alcohol occurs at 150°, while in solutions of ethyl alcohol it is at 100°. In the case of solutions of potassium iodide, dissolved in methyl and ethyl alcohols, the conductivities did not reach a zero value at the critical temperature of the solvent. Although the resistance attained considerable magnitude, the solutions still remained conductors beyond the critical temperature. Since potassium iodide is an electrolyte *per se*, this is what we would expect, according to the idea advanced by Bousfield and Lowry. Although these interesting results point to the probable correctness of the Bousfield-Lowry hypothesis, concerning the effect of temperature on the conductivity of acids and salts, nevertheless, we may fairly question whether there is enough experimental evidence to justify any general conclusion. However, there is, undoubtedly, sufficient evidence to support the idea that the effect of temperature on conductivity, over a wide range of temperature, can only be represented by inflected conductivity-temperature curves, which contain a maximum point.

The most important point in the paper of Bousfield and Lowry and one that has been generally overlooked, is the fact that the normal form of the conductivity-temperature curve, for a composite electrolyte, is an inflected curve which contains a maximum. A wide-spread impression exists, however, that an inflection in the conductivity-temperature curve indicates some abnormal change in the character of the solution. This impression has been strengthened, if indeed it has not been created, by the general adoption of a linear or parabolic formula to express the influence of temperature on conductivity. Kohlrausch makes no reference to the existence of inflected curves which contain a maximum point. Trotsch,[1] who observed inflections in the case of a number of sulphates and chlorides of copper and cobalt, regarded them as due to the decomposition of hydrates existing in the solution.

[1] Ann. d. Phys. [3], 41, 259 (1890).

Purpose of this Investigation.

Having given a brief review of what has been done on the effect of temperature on dissociation, conductivity and the temperature coefficient of conductivity, we shall now take up the work, the results of which are recorded in this paper. It is well known that different types of compounds show different degrees of dissociation and, as we have seen, the exact effect of temperature on dissociation, over the ordinary range of temperature, say from 0°–35°, has not, as yet, been fully established for any considerable number of substances. This particular problem, including its connection with other important researches along this same line, together with various hypotheses which have been proposed in recent years, is the object of this investigation. The temperature coefficients of conductivity, expressed in percentage of conductivity units, have also been worked out according to the Kohlrausch formula, and the effect of temperature on these temperature coefficients has been studied. In addition to this, the temperature coefficients, expressed in conductivity units, or increments of conductivity with rise in temperature, have been calculated and the effect of temperature on these increments has been investigated.

EXPERIMENTAL PART.

Apparatus.

The Kohlrausch method of measuring conductivity was used throughout this investigation. The bridge-wire was of "manganin" and was calibrated by the method of Strouhal and Barus.[1]

The resistance coils were standardized and found to be accurate to within 0.04 per cent.

The conductivity cells were of the form used by Jones and Lindsay.[2] They differed from the ordinary Arrhenius cells in that they were provided with a ground-glass stopper to prevent evaporation. The electrodes were cut from thick sheet platinum, and into each circular plate a stout platinum wire,

[1] Wied. Ann., 10, 326 (1880).
[2] This Journal, 28, 329 (1902).

about an inch in length, was welded. Glass tubes were sealed on to the platinum wires and electrode plates by means of sealing glass. The electrodes were then treated in the manner recommended by Whetham.[1] They were first coated with platinum black in the usual manner, and afterwards heated to a high temperature in the flame of a blast-lamp. Electrodes coated with platinum black have the property of absorbing a small amount of salt from the solution and of giving some of it up again when water, or a more dilute solution, is placed in the cell. The investigation of very dilute solutions is thus rendered less accurate. The heating process gives a gray surface, which does not absorb any appreciable quantity of salt. The oxidizing action of the platinum black is also avoided by this treatment.

The tubes carrying the electrodes, thus treated, were forced through thin rubber tubing and inserted into the glass tubes in the cell cap. Hot sealing-wax was then carefully poured over the joint, on the outside of the cap. The cell constants were determined by means of solutions of potassium chloride having a concentration 0.02 N for cells designed for concentrated solutions; for cells intended for dilute solutions a 0.002 N solution of potassium chloride was employed. Each cell was adjusted for a particular range of dilution. The adjustment was made by raising or lowering the electrodes, having first heated the sealing-wax on the cap. When the cells were finally adjusted the constants were carefully redetermined.

The determination of the cell constants was carried out in a manner somewhat different from that ordinarily employed. When a cell containing a solution is placed in a thermostat, at 25°, and allowed to come to constant temperature, air-bubbles collect around the electrodes. It is difficult to dislodge the bubbles without changing the temperature of the solution somewhat. By moving the electrodes the bubbles can be dislodged, but some minutes must elapse in order to establish temperature equilibrium before readings can be made. In the meantime more bubbles may have collected. This difficulty was avoided by first placing the cells in a zero-bath and allowing

[1] Phil. Trans., 94, [A], 321 (1900).

them to remain there about a quarter of an hour. They were then removed to the thermostat-bath at 25° and allowed to remain nearly an hour. By this mode of procedure no bubbles, or at least only a very few, collected on the electrodes. After the readings were taken the cells were allowed to remain a quarter of an hour longer, and duplicate readings were made. The second readings were nearly always identical with the first, within the limit of error of reading. The following day the whole process was repeated. With careful manipulation, cells calibrated in this manner give very accurate results and the variation in the cell constants, produced by continual use, is very small. The constants were, however, redetermined every few weeks, since small particles of platinum are liable to be removed by abrasion.

Four thermostats were used in this work, for the various temperatures ranging from 0°–35°. The zero-bath was of the type used by Jones and Lindsay,[1] though somewhat larger. It consisted of an outer and inner vessel. The inner vessel and the annular space between the two were filled with finely crushed ice. The outer portion of ice was moistened with a small quantity of distilled water, and to the ice in the inner vessel a larger amount of distilled water was added. The inner vessel contained a shelf for supporting the cells. Cells immersed in such a bath could be kept for any desired period at 0°.02–0°.05. The bath for the temperature next above zero was prepared in the following manner: A constant stream of hydrant water was passed through a large vessel, the water, being admitted at the bottom and allowed to flow out at the top, was kept thoroughly stirred by means of a small, hot-air engine. After running about an hour the temperature of the water remained almost constant. A small flame was now placed under the bath and by proper adjustment of this and of the rate of flow of the tap water, a constant temperature could be easily maintained. The 25° and 35° baths were obtained in the ordinary way and were stirred by hot-air engines. The Ostwald thermo-regulator was used and the temperature remained constant to 0°.005. The thermometers employed could

[1] This Journal, 28, 339 (1902).

be accurately read to 0°.02. The burettes and measuring flasks were carefully calibrated for 20°, according to the method of Morse and Blalock.[1]

Preparation of the Solutions.

In the preparation of the solutions, Kahlbaum's purest materials were invariably employed. These were, however, always tested for any possible impurities, which were removed. In some cases the standardization was effected by simply weighing the substance. When this was not possible the solutions were standardized by analysis. In making up a series of dilutions from the mother-solution of any substance, the temperature was, of course, kept under control and usually to within 0°.5 of the calibration temperature of the burettes and measuring flasks. The various concentrations were obtained by successive dilution, the mother-solution being the starting-point.

The water used in preparing the solutions was purified according to the method of Jones and Mackay.[2] Ordinary distilled water, after the addition of potassium bichromate and sulphuric acid, was redistilled. The distillate was distilled from acidified potassium bichromate and then, finally, from barium hydroxide. Water purified by this method gives a conductivity, at 25°, varying from 1.5 to 2.0×10^{-6}. The water correction, which must be applied to the values of the molecular conductivity at a given dilution (μ_v), usually does not attain an appreciable value until a dilution of about N/512 is reached.

Conductivity Measurements.

In making the conductivity measurements, from three to five different resistances were used for every solution. The values for the molecular conductivity (μ_v), given in the tables, are, therefore, the mean of several determinations.

Experimental Results.

In discussing the experimental results, the first substance considered is ammonium chloride. As the numerical results

[1] THIS JOURNAL, 16, 479 (1894).
[2] *Ibid.*, 19, 91 (1897).

given in each table on ammonium chloride are of considerable interest in connection with certain theoretical ideas which have been advanced in recent years, the data given in each table will be discussed separately. After a full discussion of the results with ammonium chloride, the results with the other electrolytes will be taken up in order and the data discussed collectively, because the results with the other electrolytes are of the same general character as those with ammonium chloride, except in the case of acids.

Ammonium Chloride.

The pure salt was dried by heating in an air-bath, for several hours, at 120°, after which it was placed in a desiccator until used. In making up the solutions, the exact amount of the salt necessary to make a 0.05 N solution was weighed out and introduced into a measuring flask.

Table I.—Molecular Conductivities.

v.	μ_v 0°.	μ_v 14°.5.	μ_v 25°.	μ_v 35°.
2	62.76	89.86	109.2	129.9
8	66.17	96.11	118.6	142.8
16	68.02	99.26	123.2	148.2
32	70.2	102.4	127.6	153.7
128	73.08	107.6	133.4	161.4
512	74.39	109.8	136.8	165.4
1024	74.84	110.5	137.8	167.2

In Table I. are given the values of the molecular conductivities of the various solutions of ammonium chloride at the different temperatures; v is the volume of the solution which contains a gram-molecular weight of the electrolyte and μ is the molecular conductivity at the temperature in question. The molecular conductivity increases, of course, with rise in temperature and with increase in the dilution of the solution.

Table II.—Comparisons with the Work of Kohlrausch.

	Kohlrausch.	Calculated from our work.
v.	μ_v 18°.	μ_v 18°.
2	94.8	96.3
8	...	103.6
10	103.5	...
16	...	107.2
20	107.8	...
32	...	110.8
33.3	110.1	...
100	114.2	...
128	...	116.2
500	118.0	...
512	...	118.8
1000	119.0	...
1024	...	119.6
1667	119.7	...

In Table II. is given a comparison of our results with those of Kohlrausch. The experimental results were obtained by Kohlrausch at 18°. Our work was not done at 18°. However, by applying our temperature coefficients, either in conductivity units or percentage, we can easily calculate our experimental results over to the temperature 18° and thus make comparisons with the experimental values of Kohlrausch. It is apparent, from the values given in the table, that there is a very close agreement between the two sets of results. In certain cases, where the dilutions are nearly the same, the figures are almost identical. Wherever such comparisons are made, the columns headed "calculated" are from our own results.

Table III.—Temperature Coefficients in Conductivity Units.

v.	0°–14°.5.	14°.5–25°.	25°–35°.
2	1.87	1.84	2.07
8	2.06	2.14	2.42
16	2.15	2.28	2.50
32	2.22	2.40	2.61
128	2.38	2.46	2.80
512	2.44	2.57	2.86
1024	2.46	2.60	2.94

Table III. gives the values of the temperature coefficients of conductivity expressed in conductivity units. They are calculated from the formula

$$\frac{\mu_v t_2 - \mu_v t_1}{t_2 - t_1} = \text{coefficient.}$$

Where μ_v represents the molecular conductivity, t_2 is the higher temperature and t_1 the lower temperature. The figures given are really increments of conductivity with rise in temperature. *The increments increase with rise in temperature and increase in dilution. This is always the case with salts*, while with acids, as we shall see, the increments increase with dilution, but decrease with rise in temperature. It is hardly necessary to point out the fact that these temperature coefficients are useful in calculating the conductivity of a solution of ammonium chloride at one temperature from the known conductivity at another temperature. By the aid of these temperature coefficients we can calculate conductivity values somewhat more readily than by the percentage temperature coefficients usually employed.

Table IV.—Temperature Coefficients in Per Cent.

v.	0°–14°.5.	14°.5–25°.	25°–35°.
2	2.98	2.05	1.90
8	3.11	2.23	2.02
16	3.16	2.30	2.02
32	3.16	2.34	2.04
128	3.26	2.29	2.10
512	3.29	2.34	2.09
1024	3.29	2.35	2.13

In this table the temperature coefficients of conductivity, expressed in percentage of conductivity units, are given. They are calculated according to the well-known Kohlrausch formula, expressed in the symbols used by Ostwald and others and multiplied by 100. The formula, as it was applied, is

$$\frac{\mu_v t_2 - \mu_v t_1}{t_2 - t_1} \cdot \frac{1}{\mu_v t_1} \times 100.$$

Where μ_v represents the molecular conductivity, t, is the higher and t_1 the lower temperature. The figures show that *the percentage temperature coefficients decrease with rise in temperature. The molecular conductivity increases with rise in temperature,* as was shown by Table I., but the *percentage of increase decreases.* This fact is especially interesting when considered in connection with the next table.

Table V.—Percentage Dissociation.

v.	α 0°.	α 14°.5.	α 25°.	α 35°.
2	84.0	81.3	79.2	77.7
8	88.4	87.0	86.1	85.4
16	90.8	89.8	89.4	88.6
32	93.8	92.7	92.6	91.9
128	97.6	97.4	96.8	96.5
512	99.4	99.4	99.3	98.9
1024	100.0	100.0	100.0	100.0

Table V. gives the values of α, the percentage of dissociation, of ammonium chloride at the various temperatures for the different dilutions. α is calculated from the formula

$$\alpha = \frac{\mu_v}{\mu\infty} \times 100,$$

where μ_v represents the molecular conductivity and $\mu\infty$ the molecular conductivity at complete dissociation. In this case

$$\mu\infty = \mu_v \text{ at } 1024 \text{ liters.}$$

It is apparent, from the table, that *the percentage of dissociation decreases with rise in temperature.* As the temperature increases from 0° to 35°, the values of α decrease, except in the most dilute solutions, where the salt is completely, or almost completely dissociated. Of course, here we should not expect to notice a large decrease, except over a wide range of temperature.

Ammonium Bromide.

The pure salt was heated in an air-bath, for several hours, at 120°, after which it was dried in a desiccator for some days. The mother-solution was prepared by direct weighing; the other solutions were made by diluting the original one. As is shown by the numerical values given in the tables, the same kind of results are obtained with ammonium bromide as with ammonium chloride. In Table VI. the molecular conductivities are seen to increase with rise in temperature. Table VII. shows that the temperature coefficients of conductivity, expressed in conductivity units, increase with temperature. In Table VIII. the percentage temperature coefficients of conductivity decrease with rise in temperature, and Table IX. shows a decrease in dissociation with rise in temperature.

No table is given for ammonium bromide, which shows how our values of the molecular conductivities, calculated by means of the temperature coefficients, compare with those obtained experimentally by other investigators. It was not considered necessary in each case to include these tables, as a few will suffice to show the general agreement.

Table VI.—Molecular Conductivities.

v.	μ_v 0°.	μ_v 12°.5.	μ_v 25°.	μ_v 35°.
2	67.26	89.81	115.1	136.7
8	69.36	95.44	123.6	146.8
16	71.53	98.06	127.4	153.3
32	73.50	101.1	131.7	158.0
128	76.18	105.5	137.9	165.0
512	77.55	107.8	141.3	168.9
1024	77.06	107.5	140.9	169.5

Table VII.—Temperature Coefficients in Conductivity Units.

v.	0°–12°.5.	12°.5–25°.	25°–35°.
2	1.80	2.02	2.16
8	2.09	2.25	2.32
16	2.12	2.35	2.59
32	2.21	2.45	2.63
128	2.35	2.59	2.71
512	2.42	2.68	2.76
1024	2.43	2.67	2.86

Table VIII.—Temperature Coefficients in Per Cent.

v.	0°–12°.5.	12°.5–25°.	25°–35°.
2	2.68	2.25	1.88
8	3.01	2.36	1.88
16	2.96	2.40	2.03
32	3.01	2.42	2.00
128	3.08	2.46	1.98
512	3.12	2.49	1.95
1024	3.16	2.49	2.03

Table IX.—Percentage Dissociation.

v.	α 0°.	α 12°.5.	α 25°.	α 35°.
2	87.3	83.5	81.7	80.6
8	90.0	88.8	87.7	86.6
16	92.8	91.2	90.4	90.4
32	95.4	94.1	93.5	93.2
128	98.9	98.1	97.9	97.3
512	100.0	100.0	100.0	99.6
1024	100.0	100.0	100.0	100.0

Sodium Bromide.

The salt was dried by heating for several hours, at 120°, after which it was placed in a desiccator until used. The mother-solution was made up by direct weighing and the other solutions obtained by dilution. Conductivity measurements were made at only three different temperatures. However, results of the same character were obtained as with the preceding salts. Ostwald has measured the conductivities of a few dilutions of sodium bromide, at 25°. His results are included in Table X. A comparison of the two series of results shows a close agreement.

Table X.—Molecular Conductivities.

v.	μ_v 0°.	μ_v 11°.8.	μ_v 25°.	Ostwald. μ_v 25°.
2	51.46	69.24	91.9	...
8	55.36	75.26	100.3	...
16	57.35	78.17	105.1	...
32	58.79	80.03	107.7	107.9
128	61.23	84.35	113.3	113.8
512	63.02	87.17	116.8	118.6
2048	64.48	89.34	121.1	119.9

Table XI.—Temperature Coefficients in Conductivity Units.

v.	0°–11°.8.	11°.8–25°.
2	1.50	1.72
8	1.69	1.90
16	1.76	2.04
32	1.80	2.10
128	1.96	2.19
512	2.04	2.24
2048	2.11	2.40

Table XII.—Temperature Coefficients in Per Cent.

v.	0°–11°.8.	11°.8–25°.
2	2.91	2.48
8	3.05	2.52
16	3.07	2.61
32	3.06	2.62
128	3.20	2.60
512	3.24	2.57
2048	3.27	2.69

Table XIII.—Percentage Dissociation.

v.	α 0°.	α 11°.8.	α 25°.
2	79.8	77.5	75.9
8	85.9	84.2	82.8
16	88.9	87.5	86.8
32	91.2	89.6	88.9
128	95.0	94.4	93.6
512	97.7	97.6	96.4
2048	100.0	100.0	100.0

Sodium Iodide.

The salt was dried by heating, for some hours, at 120° and then placed in a desiccator until used. The original solution was made up by direct weighing and the other solutions by diluting. As is shown by the numerical values given in the tables, the effect of temperature on conductivity and dissociation is the same as with the other salts.

Table XIV.—Molecular Conductivities.

v.	μ_v 0°.	μ_v 16°.	μ_v 25°.	μ_v 35°.
2	51.90	77.22	92.73	111.6
8	55.26	83.52	100.4	121.6
16	57.03	86.36	104.2	125.8
32	58.62	89.02	107.4	130.6
128	60.97	93.20	112.5	136.8
512	61.81	94.91	114.7	139.3
1024	63.14	96.28	116.4	141.8
2048	64.51	98.4	119.1	144.5

Table XV.—Temperature Coefficients in Conductivity Units.

v.	0°–16°.	16°–25°.	25°–35°.
2	1.58	1.72	1.88
8	1.77	1.88	2.12
16	1.83	1.98	2.16
32	1.90	2.04	2.32
128	2.01	2.14	2.43
512	2.07	2.20	2.46
1024	2.07	2.24	2.54
2048	2.12	2.30	2.54

Table XVI.—Temperature Coefficients in Per Cent.

v.	0°–16°.	16°–25°.	25°–35°.
2	3.04	2.23	2.03
8	3.20	2.25	2.11
16	3.21	2.29	2.07
32	3.24	2.29	2.16
128	3.30	2.30	2.16
512	3.35	2.32	2.14
1024	3.28	2.33	2.18
2048	3.29	2.34	2.13

Table XVII.—Percentage Dissociation.

v.	α 0°.	α 16°.	α 25°.	α 35°.
2	80.5	78.5	77.9	77.2
8	85.7	84.9	84.3	84.2
16	88.4	87.8	87.5	87.1
32	90.9	90.5	90.2	90.4
128	94.5	94.7	94.5	94.7
512	95.8	96.5	96.3	96.4
1024	97.9	97.8	97.7	98.1
2048	100.0	100.0	100.0	100.0

Sodium Carbonate.

The salt was dried for some hours, at 120° and then kept in a desiccator until used. Conductivity measurements were made at only three temperatures. In Table XIX. is given a comparison of the results obtained by Kohlrausch at 18°, with the values of the molecular conductivities calculated by means of the temperature coefficients between 15°.3 and 25°. As is shown by the table, there is a close agreement between the two sets of results.

Table XVIII.—Molecular Conductivities.

v.	μ_v 0°.	μ_v 15°.3.	μ_v 25°.
2	50.99	78.94	100.4
8	70.7	109.1	137.8
16	79.75	123.8	155.4
32	87.28	134.7	170.8
128	99.16	155.4	197.9
512	105.8	166.9	209.6
1024	110.8	173.9	218.1

Table XIX.—Comparison with the Work of Kohlrausch.

	Kohlrausch.	Calculated.
v.	μ_v 18°.	μ_v 18°.
2	85.4	84.91
4	102.0	. .
8	. .	117.09
16	. .	132.6
20	136.4	. .
32	. .	144.7
40	150.2	. .
128	. .	167.2
200	179.8	. .

Table XX.—Temperature Coefficients in Conductivity Units.

v.	0°–15°.3.	15°.3–25°.
2	1.83	2.21
8	2.51	2.96
16	2.88	3.26
32	3.10	3.72
128	3.67	4.38
512	3.99	4.40
1024	4.12	4.56

Table XXI.—Temperature Coefficients in Per Cent.

v.	0°-15°.3.	15°.3-25°.
2	3.59	2.80
8	3.55	2.71
16	3.61	2.64
32	3.55	2.77
128	3.70	2.82
512	3.77	2.64
1024	3.72	2.62

Table XXII.—Percentage Dissociation.

v.	α 0°.	α 15°.3.	α 25°.
2	46.0	45.4	46.0
8	63.8	62.7	63.2
16	72.0	71.2	71.3
32	78.8	77.5	78.3
128	89.5	89.4	90.7
512	95.5	95.9	96.1
1024	100.0	100.0	100.0

Sodium Acetate.

The sodium acetate used was a specimen of the fused salt, obtained from Kahlbaum. After purification it was dried in an air-bath, for several days, at 120°. This treatment was necessary to bring it to constant weight. The original solution was made up by weight. Results of the same general character were obtained with sodium acetate as with the other salts.

The temperature coefficients, in conductivity units, are small, as might be expected from the comparatively small conductivity of the salt.

Table XXIII.—Molecular Conductivities.

v.	μ_v 0°.	μ_v 13°.6.	μ_v 25°.	μ_v 35°.
2	28.39	41.93	54.86	67.06
8	34.30	50.73	66.25	81.09
16	36.37	53.86	70.17	86.01
32	38.11	56.59	73.81	90.55
128	40.41	60.22	78.32	96.43
512	41.21	61.63	80.14	99.34
1024	40.65	61.15	79.12	98.6
2048	41.28	61.97	80.14	99.4

Table XXIV.—Temperature Coefficients in Conductivity Units.

v.	0°–13°.6.	13°.6–25°.	25°–35°.
2	0.996	1.13	1.22
8	1.21	1.36	1.48
16	1.29	1.43	1.58
32	1.36	1.51	1.67
128	1.46	1.59	1.81
512	1.50	1.62	1.92
1024	1.51	1.58	1.95
2048	1.52	1.59	1.93

Table XXV.—Temperature Coefficients in Per Cent.

v.	0°–13°.6.	13°.6–25°.	25°–35°.
2	3.51	2.69	2.22
8	3.53	2.68	2.23
16	3.52	2.66	2.25
32	3.57	2.67	2.26
128	3.61	2.64	2.31
512	3.67	2.63	2.38
1024	3.71	2.58	2.46
2048	3.68	2.57	2.41

Table XXVI.—Percentage Dissociation.

v.	α 0°.	α 13°.6.	α 25°.	α 35°.
2	68.9	67.9	68.5	67.5
8	83.2	82.3	82.7	81.6
16	88.3	87.4	87.6	86.6
32	92.2	91.8	92.1	91.2
128	98.1	97.7	97.7	97.1
512	100.0	100.0	100.0	100.0

Potassium Chloride.

The salt was recrystallized 5 times. It was then dried for several days, in an air-bath, at 150° and afterwards preserved in a desiccator until used. Conductivity measurements were made at 5 different temperatures. In Table XXVIII., the calculated values of the molecular conductivities, at 18°, show a very close agreement with those obtained experimentally by Kohlrausch at the same temperature.

Table XXVII.—Molecular Conductivities.

v.	μ_v 0°.	μ_v 4°.3.	μ_v 15°.5.	μ_v 25°.	μ_v 35°.
2	62.96	70.09	91.09	109.5	130.8
8	66.47	74.48	98.24	118.6	142.5
16	68.4	76.95	101.5	122.9	147.7
32	70.27	78.95	104.9	126.8	152.5
128	73.0	82.25	109.4	132.4	159.9
512	74.24	83.59	111.9	135.5	163.0
1024	75.14	84.59	112.9	137.0	165.4

Table XXVIII.—Comparison with the Work of Kohlrausch.

	Kohlrausch.	Calculated.
v.	μ_v 18°.	μ_v 18°.
2	95.8	95.9
8	...	103.6
10	104.7	...
16	...	107.0
20	108.3	...
32	...	110.7
33.3	110.7	...
100	114.7	...
128	...	115.5
500	118.5	...
512	...	118.1
1000	119.3	...
1024	...	119.3
1667	119.9	...

Table XXIX.—Temperature Coefficients in Conductivity Units.

v.	0°–4°.3.	4°.3–15°.5.	15°.5–25°.	25°–35°.
2	1.66	1.88	1.94	2.13
8	1.86	2.12	2.14	2.39
16	1.99	2.19	2.25	2.48
32	2.02	2.32	2.31	2.57
128	2.15	2.42	2.42	2.75
512	2.17	2.53	2.48	2.75
1024	2.20	2.53	2.54	2.84

Table XXX.—Temperature Coefficients in Per Cent.

v.	0°-4°.3.	4°.3-15°.5.	15°.5-25°.	25°-35°.
2	2.63	2.68	2.13	1.94
8	2.78	2.80	2.18	2.01
16	2.91	2.85	2.22	2.02
32	2.87	2.94	2.20	2.03
128	2.94	2.94	2.21	2.08
512	2.92	3.03	2.22	2.03
1024	2.93	2.99	2.25	2.07

Table XXXI.—Percentage Dissociation.

v.	α 0°.	α 4°.3.	α 15°.5.	α 25°.	α 35°.
2	83.8	82.9	80.7	79.9	79.0
8	88.5	88.0	87.0	86.6	86.2
16	91.0	91.0	89.9	89.7	89.3
32	93.5	93.3	92.0	92.6	92.2
128	97.2	97.2	96.9	96.6	96.7
512	98.8	98.8	99.1	98.9	98.5
1024	100.0	100.0	100.0	100.0	100.0

Potassium Bromide.

The sample of potassium bromide, which was used, was prepared in the same manner as the preceding salts. It was dried for some hours, in an air-bath, at 110° and then placed in a desiccator until used. In Table XXXIII. is given a comparison of our calculated results with those obtained experimentally by Krannhals, at 18°. The two series of values agree very closely. The same general rule holds for dissociation and temperature coefficients, as has been observed with the preceding compounds.

Table XXXII.—Molecular Conductivities.

v.	μ_v 0°.	μ_v 14°.5.	μ_v 25°.	μ_v 35°.
2	65.82	93.21	114.4	136.2
8	68.01	98.45	121.3	145.6
16	70.1	101.7	125.2	150.5
32	71.84	104.6	128.8	154.6
128	74.79	109.0	134.5	162.0
512	75.73	111.3	137.6	165.5
1024	79.23	115.6	143.5	172.6

Table XXXIII.—Comparison with the Work of Krannhals.

	Krannhals.	Calculated.
v.	μ_v 18°.	μ_v 18°.
2	98.2	100.3
8	105.7	106.1
16	110.0	109.5
32	113.0	112.7
128	117.0	117.5
256	118.8	...
512	...	120.1
1000	121.0	...
1024	...	124.9

Table XXXIV.—Temperature Coefficients in Conductivity Units.

v.	0°–14°.5.	14°.5–25°.	25°–35°.
2	1.89	2.02	2.18
8	2.10	2.18	2.43
16	2.18	2.24	2.53
32	2.26	2.30	2.58
128	2.35	2.43	2.75
512	2.45	2.50	2.79
1024	2.51	2.66	2.91

Table XXXV.—Temperature Coefficients in Per Cent.

v.	0°–14°.5.	14°.5–25°.	25°–35°.
2	2.87	2.17	1.90
8	3.09	2.21	2.00
16	3.07	2.20	2.02
32	3.15	2.20	2.00
128	3.14	2.23	2.04
512	3.24	2.25	2.03
1024	3.17	2.30	2.03

Table XXXVI.—Percentage Dissociation.

v.	α 0°.	α 14°.5.	α 25°.	α 35°.
2	83.1	80.6	79.7	78.9
8	85.8	85.2	84.5	84.4
16	88.5	88.0	87.2	87.2
32	90.8	90.5	89.8	89.6
128	94.4	94.3	93.7	93.9
512	95.6	96.3	95.9	95.9
1024	100.0	100.0	100.0	100.0

Potassium Iodide.

The potassium iodide was dried for several hours, at 110°. The original solution was made up by direct weighing. In Table XXXVIII. the comparisons of our figures for the molecular conductivities with the work of others, show close agreement. In some cases where the dilutions are the same, or very nearly the same, the numerical values are almost identical.

Table XXXVII.—Molecular Conductivities.

v.	μ_v 0°.	μ_v 10°.1.	μ_v 25°.	μ_v 35°.
2	65.78	83.88	112.8	133.7
8	68.45	88.18	120.7	144.5
16	70.17	90.51	124.5	148.4
32	71.90	93.32	128.0	153.0
128	74.41	96.67	133.7	160.2
512	76.35	98.91	137.3	165.9
1024	77.77	101.9	141.8	170.9
2048	79.2	104.9	147.2	177.2

Table XXXVIII.—Comparison with the Work of Others.

Ostwald.		Kohlrausch.		Calculated.
v.	μ_v 25°.	v.	μ_v 18°.	μ_v 18°.
	...	2	99.7	99.2
	...	8	...	105.4
	...	10	106.9	...
32	128.5	16	...	108.5
128	135.4	20	110.2	...
512	139.6	32	...	111.7
1024	140.7	33.3	112.3	...
	...	128	...	116.3
	...	166.7	117.6	...
	...	500	119.7	...
	...	512	...	119.2
	...	1000	120.3	...
	...	1024	...	123.0

Table XXXIX.—Temperature Coefficients in Conductivity Units.

v.	0°–10°.1.	10°.1–25°.	25°–35°.
2	1.79	1.94	2.09
8	1.95	2.18	2.38
16	2.01	2.28	2.39
32	2.12	2.33	2.50
128	2.20	2.48	2.65
512	2.23	2.58	2.86
1024	2.39	2.68	2.91
2048	2.54	2.84	3.00

Table XL.—Temperature Coefficients in Per Cent.

v.	0°–10°.1.	10°.1–25°.	25°–35°.
2	2.72	2.31	1.85
8	2.84	2.47	1.97
16	2.86	2.52	1.92
32	2.95	2.50	1.95
128	2.96	2.57	1.98
512	2.92	2.61	2.08
1024	3.07	2.63	2.05
2048	3.21	2.71	2.04

Table XLI.—Percentage Dissociation.

v.	α 0°.	α 10°.1.	α 25°.	α 35°.
2	83.1	80.0	76.6	75.5
8	86.4	84.1	82.0	81.5
16	88.6	86.3	84.6	83.7
32	90.8	89.0	87.0	86.3
128	94.0	92.1	90.8	90.4
512	96.4	94.3	93.3	93.6
1024	98.2	97.1	96.3	96.4
2048	100.0	100.0	100.0	100.0

Potassium Nitrate.

The specimen of potassium nitrate used was dried for 2 days, at 110° and then placed in a desiccator until used. The mother-solution was standardized by direct weighing. The comparisons of the molecular conductivities given in Table XLIII. show that our calculated values are practically the mean of those obtained experimentally by Kohlrausch and Krannhals, except in the very dilute solutions, where our values agree closely with those obtained by Kohlrausch.

Table XLII.—Molecular Conductivities.

v.	μ_v 0°.	μ_v 10°.	μ_v 25°.	μ_v 35°.
2	54.02	69.67	95.21	113.8
8	61.94	80.22	111.0	132.4
16	65.33	84.31	116.3	139.0
32	67.92	87.78	121.3	145.0
128	72.05	93.57	129.5	154.1
512	76.34	98.71	137.0	163.9
1024	76.31	99.8	139.6	166.7

Table XLIII.—Comparison with the Work of Others.

	Kohlrausch.	Calculated.	Krannhals.
v.	μ_v 18°.	μ_v 18°.	μ_v 18°.
2	83.9	83.3	83.1
8	...	96.6	95.6
10	103.7	...	...
16	...	101.4	100.3
20	106.7	...	...
32	...	105.7	104.3
100	114.0	...	...
128	...	112.7	109.3
500	118.0	...	...
512	...	119.2	...
1000	119.0	...	114.0
1024	...	121.1	...

Table XLIV.—Temperature Coefficients in Conductivity Units.

v.	0°–10°.	10°–25°.	25°–35°.
2	1.56	1.70	1.86
8	1.83	2.05	2.14
16	1.90	2.13	2.27
32	1.99	2.23	2.37
128	2.15	2.40	2.46
512	2.24	2.55	2.69
1024	2.35	2.65	2.71

Table XLV.—Temperature Coefficients in Per Cent.

v.	0°–10°.	10°–25°.	25°–35°.
2	2.89	2.44	1.95
8	2.95	2.56	1.93
16	2.91	2.53	1.91
32	2.93	2.54	1.95
128	2.98	2.56	1.82
512	2.93	2.58	1.96
1024	3.08	2.65	1.94

Table XLVI.—Percentage Dissociation.

v.	α 0°.	α 10°.	α 25°.	α 35°.
2	70.8	69.8	68.2	68.3
8	81.2	80.4	79.5	79.4
16	85.6	84.5	83.3	83.4
32	89.0	88.0	86.9	87.0
128	94.4	93.8	92.8	92.4
512	100.0	98.9	98.1	98.3
1024	100.0	100.0	100.0	100.0

Potassium Sulphate.

The specimen of salt used was dried for some hours, at 120° and then kept in a desiccator until used. The comparison of the molecular conductivities given in Table XLVIII. are not quite as close as in the case of certain other salts.

The temperature coefficients in conductivity units are large and the conductivity of the salt itself is comparatively large.

Table XLVII.—Molecular Conductivities.

v.	μ_v 0°.	μ_v 9°.5.	μ_v 25°.	μ_v 35°.
2	87.19	110.1	152.6	180.7
8	101.9	130.5	183.6	219.8
16	109.9	140.9	199.2	238.4
32	117.9	151.5	214.4	256.9
128	131.9	170.3	242.1	291.0
512	142.7	184.0	263.5	318.4
1024	145.0	187.0	268.0	325.0

Table XLVIII.—Comparison with the Work of Kohlrausch.

v.	Kohlrausch. μ_v 18°.	Calculated. μ_v 18°.
2	134.4	133.4
4	147.2	...
8	...	159.6
16	...	172.9
20	179.4	...
32	...	186.0
40	191.8	...
128	...	209.7
200	219.6	...
512	...	227.6
1000	236.2	...
1024	...	231.4
2000	241.4	...

Table XLIX.—Temperature Coefficients in Conductivity Units.

v.	0°–9°.5.	9°.5–25°.	25°–35°.
2	2.41	2.74	2.81
8	3.01	3.43	3.62
16	3.26	3.76	3.92
32	3.54	4.06	4.25
128	4.04	4.63	4.89
512	4.35	5.13	5.49
1024	4.42	5.23	5.70

Table L.—Temperature Coefficients in Per Cent.

v.	0°–9°.5.	9°.5–25°.	25°–35°.
2	2.76	2.49	1.84
8	2.95	2.63	1.91
16	2.97	2.67	1.97
32	3.00	2.61	1.98
128	3.06	2.72	2.03
512	3.05	2.79	2.08
1024	3.05	2.79	2.13

Table LI.—Percentage Dissociation.

v.	α 0°.	α 9°.5.	α 25°.	α 35°.
2	60.1	58.9	56.9	55.6
8	70.3	69.8	68.5	67.6
16	75.8	75.4	74.3	73.4
32	81.3	81.0	80.0	79.1
128	91.0	91.0	90.3	89.5
512	98.4	98.4	98.3	98.0
1024	100.0	100.0	100.0	100.0

Potassium Bisulphate.

The sample of salt was dried for several hours, at 110° and preserved in a desiccator until used. The original solution was made up by direct weighing. Here, again, we find the same phenomena that have appeared in the preceding cases; the percentage temperature coefficients of conductivity and the percentage dissociation decrease with rise in temperature.

The temperature coefficients in conductivity units are very large and the conductivity of the salt itself is very large, because it is an acid salt and splits off the swift hydrogen ion.

Table LII.—Molecular Conductivities.

v.	μ_v 0°.	μ_v 12°.5.	μ_v 25°.	μ_v 35°.
2	153.8	184.0	207.6	220.6
8	182.1	222.9	254.2	274.1
16	201.2	248.8	286.6	310.0
32	223.6	280.7	323.7	353.1
128	263.1	336.9	401.0	446.4
512	291.8	383.9	467.1	531.0
2048	290.9	385.8	478.2	556.6
8192	291.2	401.0	496.0	569.0

Table LIII.—Temperature Coefficients in Conductivity Units.

v.	0°–12°.5.	12°.5–25°.	25°–35°.
2	2.42	1.89	1.30
8	3.82	2.50	1.99
16	3.81	3.02	2.34
32	4.57	3.44	2.94
128	5.90	5.13	4.54
512	7.37	6.66	6.39
2048	7.59	7.39	7.84
8192	8.78	7.60	7.30

Table LIV.—Temperature Coefficients in Per Cent.

v.	0°–12°.5.	12°.5–25°.	25°–35°.
2	1.57	1.03	0.63
8	2.10	1.12	0.78
16	1.89	1.21	0.82
32	2.04	1.23	0.91
128	2.24	1.52	1.13
512	3.21	1.73	1.37
2048	2.61	1.92	1.64
8192	3.01	1.89	1.47

Table LV.—Percentage Dissociation.

v.	α 0°.	α 12°.5.	α 25°.	α 35°.
2	52.8	45.9	41.9	38.8
8	62.5	55.6	51.3	48.2
16	69.1	62.0	57.8	54.5
32	76.8	70.0	65.3	62.1
128	90.3	84.0	80.8	78.5
512	100.0	95.7	94.2	93.3
2048	100.0	96.2	96.4	97.6
8192	100.0	100.0	100.0	100.0

Potassium Carbonate.

The salt was dried, for some hours, at 110°. The solutions were made up by direct weighing and dilution. The comparisons given in Table LVII. are not quite so concordant as in preceding cases. The conductivity measurements were made at only 3 temperatures.

Table LVI.—Molecular Conductivities.

v.	μ_v 0°.	μ_v 17°.8.	μ_v 25°.
2	84.34	129.2	150.1
8	98.74	154.1	180.9
16	105.3	166.5	195.3
32	112.9	179.6	210.5
128	122.3	197.6	233.6
512	131.2	211.1	250.1

Table LVII.—Comparison with the Work of Kohlrausch.

	Kohlrausch.	Calculated.
v.	μ_v 18°.	μ_v 18°.
2	132.0	129.8
4	145.6	...
8	...	154.8
16	...	167.3
20	175.8	...
32	...	180.5
40	188.4	...
512	...	212.2
1000	239.8	...

Table LVIII.—Temperature Coefficients in Conductivity Units.

v.	0°–17°.8.	17°.8–25°.
2	2.52	2.90
8	3.11	3.72
16	3.44	4.00
32	3.75	4.29
128	4.23	5.00
512	4.49	5.42

Table LIX.—Temperature Coefficients in Per Cent.

v.	0°–17°.8.	17°.8–25°.
2	2.99	2.24
8	3.15	2.41
16	3.26	2.40
32	3.32	2.39
128	3.46	2.53
512	3.42	2.57

Table LX.—Percentage Dissociation.

v.	α 0°.	α 17°.8.	α 25°.
2	64.3	61.2	60.0
8	75.3	73.0	72.3
16	80.3	78.9	78.1
32	86.0	85.1	84.2
128	93.2	93.6	93.4
512	100.0	100.0	100.0

Potassium Ferrocyanide.

The sample of potassium ferrocyanide used was purified by repeated crystallization. The mother-solution was made up by direct weighing and the others obtained by dilution. In this case the effect of temperature on dissociation is very slight. The dissociation at 35° is 2 per cent less than at 0°, in a 0.25 N solution, showing a small, but distinct temperature effect in the more concentrated solutions. As we have seen, the decrease in dissociation with rise in temperature becomes greater as the concentration of the solution is increased. This salt is, therefore, no exception to the rule.

The temperature coefficients in conductivity units are the largest thus far met with, and the conductivity of the salt is very great, on account of the large number of ions into which it dissociates. The values of μ_v that are taken as $\mu\infty$ are probably somewhat too small, but they are the best that can be obtained in the circumstances.[1]

[1] Jones and Bassett: THIS JOURNAL, 34, 313 (1905).

Table LXI.—Molecular Conductivities.

v.	μ_v 0°.	μ_v 13°.1.	μ_v 25°.	μ_v 35°.
4	162.1	224.1	287.1	341.8
8	168.8	236.8	305.1	364.5
16	179.9	255.0	327.1	394.1
32	195.6	277.0	357.8	430.7
128	236.1	335.5	432.8	523.8
512	280.7	399.4	516.6	627.0
1024	295.1	421.4	546.5	660.0
2048	315.0	449.0	578.0	703.0
8192	328.0	467.0	599.0	724.0

Table LXII.—Temperature Coefficients in Conductivity Units.

v.	0°–13°.1.	13°.1–25°.	25°–35°.
4	4.73	5.29	5.47
8	5.19	5.74	5.94
16	5.73	6.06	6.70
32	6.21	6.79	7.29
128	7.59	8.18	9.10
512	9.06	9.85	11.04
1024	9.64	10.51	11.35
2048	10.23	10.84	12.50
8192	10.61	11.09	12.50

Table LXIII.—Temperature Coefficients in Per Cent.

v.	0°–13°.1.	13°.1–25°.	25°–35°.
4	2.91	2.36	1.91
8	3.08	2.42	1.62
16	3.19	2.38	2.05
32	3.17	2.45	2.04
128	3.21	2.44	2.10
512	3.22	2.47	2.14
1024	3.27	2.49	2.08
2048	3.24	2.41	2.16
8192	3.23	2.37	2.09

Table LXIV.—Percentage Dissociation.

v.	α 0°.	α 13°.1.	α 25°.	α 35°.
4	49.4	48.0	47.9	47.2
8	51.5	50.7	50.9	50.3
16	54.8	54.6	54.6	54.4
32	59.6	59.3	59.7	59.5
128	72.0	71.8	72.3	72.3
512	85.6	85.5	86.2	86.6
1024	90.0	90.2	91.2	91.2
2048	96.0	96.1	96.4	97.1
8192	100.0	100.0	100.0	100.0

Calcium Chloride.

The salt was dissolved in water and the strength of the solution determined by analysis, the calcium being weighed as calcium sulphate.

The temperature coefficients, in conductivity units, are large, as is the conductivity of the salt itself. The salt may show slight hydrolysis, which would affect the value of $\mu\infty$.

Table LXV.—Molecular Conductivities.

v.	μ_v 0°.	μ_v 11°.5.	μ_v 25°.	μ_v 35°.
2	89.32	119.7	159.2	190.3
8	105.5	147.8	193.4	233.8
16	112.3	157.5	207.4	250.1
32	118.5	163.4	219.9	266.0
128	129.9	179.8	243.6	295.0
512	138.2	192.1	260.8	316.4
1024	137.8	191.8	261.2	317.3

Table LXVI.—Temperature Coefficients in Conductivity Units.

v.	0°–11°.5.	11°.5–25°.	25°–35°.
2	2.64	2.93	3.11
8	3.68	3.38	4.04
16	3.93	3.70	4.27
32	3.90	4.18	4.61
128	4.34	4.73	5.14
512	4.69	5.09	5.56
1024	4.70	5.14	5.61

Table LXVII.—Temperature Coefficients in Per Cent.

v.	0°–11°.5.	11°.5–25°.	25°–35°.
2	2.96	2.45	1.95
8	3.49	2.29	2.09
16	3.50	2.33	2.06
32	3.29	2.56	2.10
128	3.34	2.63	2.11
512	3.39	2.65	2.13
1024	3.41	2.68	2.15

Table LXVIII.—Percentage Dissociation.

v.	α 0°.	α 11°.5.	α 25°.	α 35°.
2	64.8	62.4	60.9	60.0
8	76.6	77.1	74.0	73.7
16	81.5	82.1	79.4	78.8
32	85.9	85.1	84.2	83.8
128	94.3	93.7	93.3	93.0
512	100.0	100.0	99.8	99.7
1024	100.0	100.0	100.0	100.0

Calcium Bromide.

The mother-solution of calcium bromide was standardized by analysis. The calcium was determined as the sulphate. We have, in this case, the same general temperature effect as that already noted for other substances. The percentage temperature coefficients of conductivity and the percentage dissociation decrease with rise in temperature.

The same remarks apply to the temperature coefficients in conductivity units and to the conductivity itself, as in the case of calcium chloride.

Table LXIX.—Molecular Conductivities.

v.	μ_v 0°.	μ_v 14°.4.	μ_v 25°.	μ_v 35°.
2	85.95	122.7	151.0	181.1
8	97.74	144.0	177.5	214.8
16	103.0	150.5	188.4	227.6
32	108.2	158.4	199.0	240.5
128	117.3	173.3	217.9	265.0
512	122.9	182.0	229.7	278.5
1024	126.3	186.9	236.5	286.5
2048	126.8	188.2	239.5	291.5

Table LXX.—Temperature Coefficients in Conductivity Units.

v.	0°–14°.4.	14°.4–25°.	25°–35°.
2	2.55	2.67	3.01
8	3.21	3.16	3.73
16	3.30	3.58	3.92
32	3.49	3.83	4.15
128	3.89	4.21	4.71
512	4.10	4.50	4.88
1024	4.21	4.68	5.00
2048	4.26	4.84	5.20

Table LXXI.—Temperature Coefficients in Per Cent.

v.	0°–14°.4.	14°.4–25°.	25°–35°.
2	2.97	2.18	1.99
8	3.28	2.19	2.10
16	3.20	2.37	2.08
32	3.23	2.42	2.09
128	3.32	2.43	2.16
512	3.34	2.47	2.13
1024	3.33	2.50	2.11
2048	3.36	2.57	2.17

Table LXXII.—Percentage Dissociation.

v.	α 0°.	α 14°.4.	α 25°.	α 35°.
2	67.7	65.2	63.1	62.1
8	77.1	76.5	74.1	73.7
16	81.2	80.0	78.7	78.1
32	85.3	84.2	83.1	82.5
128	92.5	92.1	91.0	90.9
512	96.9	96.7	95.9	95.5
1024	99.6	99.3	98.7	98.3
2048	100.0	100.0	100.0	100.0

Strontium Bromide.

The strength of the original solution was determined by analysis, the strontium being weighed as the sulphate.

Table LXXIII.—Molecular Conductivities.

v.	μ_v 0°.	μ_v 13°.5.	μ_v 25°.	μ_v 35°.
2	88.03	122.1	153.8	183.1
8	100.0	141.8	180.6	217.2
16	103.7	148.1	190.0	228.1
32	110.0	157.2	202.2	243.9
128	117.8	170.6	219.1	267.1
512	128.8	185.4	239.1	289.9
1024	129.1	186.6	239.6	292.3

Table LXXIV.—Temperature Coefficients in Conductivity Units.

v.	0°–13°.5.	13°.5–25°.	25°–35°.
2	2.52	2.76	2.93
8	3.10	3.37	3.66
16	3.29	3.64	3.81
32	3.50	3.91	4.17
128	3.91	4.22	4.80
512	4.19	4.67	5.08
1024	4.26	4.61	5.27

Table LXXV.—Temperature Coefficients in Per Cent.

v.	0°–13°.5.	13°.5–25°.	25°–35°.
2	2.86	2.26	1.91
8	3.10	2.38	2.03
16	3.17	2.46	2.01
32	3.18	2.49	2.06
128	3.32	2.17	2.19
512	3.25	2.52	2.13
1024	3.30	2.47	2.20

Table LXXVI.—Percentage Dissociation.

v.	α 0°.	α 13°.5.	α 25°.	α 35°.
2	68.2	65.4	64.2	62.6
8	77.5	76.0	75.4	74.3
16	80.3	79.4	79.3	78.0
32	85.2	84.2	84.4	83.4
128	91.2	91.4	91.4	91.4
512	99.8	99.4	99.8	99.2
1024	100.0	100.0	100.0	100.0

Barium Chloride.

The sample of barium chloride was dried in an air-bath, for some hours, at 110°. The mother-solution was made up by direct weighing and the lesser concentrations obtained by dilution. The conductivity measurements were made at 5 different temperatures. In Table LXXIV., the calculated values of the molecular conductivities, at 18°, show a close agreement with those obtained, experimentally, by Kohlrausch and Krannhals, at the same temperature. In the case of dilute solutions, however, our values are somewhat lower.

Table LXXVII.—Molecular Conductivities.

v.	μ_v 0°.	μ_v 4°.6.	μ_v 16°.5.	μ_v 25°.	μ_v 35°.
2	86.62	96.61	128.2	150.0	178.6
8	99.06	112.3	151.1	179.0	215.3
16	105.2	119.5	161.2	191.6	230.4
64	116.2	132.4	180.2	215.2	260.3
256	125.1	142.7	194.7	232.9	282.6
512	126.5	144.3	197.2	235.5	286.2
1024	130.9	149.3	203.8	243.4	296.4
2048	132.7	151.2	206.3	247.1	300.5

Table LXXVIII.—Comparison with Work of Others.

	Kohlrausch.	Krannhals.	Calculated.
v.	μ_v 18°.	μ_v 18°.	μ_v 18°.
2	131.6	131.0	132.0
8	...	154.0	156.0
16	...	163.0	166.6
20	172.2	....	...
32	...	170.0	...
40	180.8	...	...
64	...	...	186.4
66.7	187.8	...	...
128	...	192.0	...
200	201.2	...	...
256	...	...	201.4
333	206.2	...	...
512	...	212.0	204.0
1000	214.8	...	...
1024	...	...	211.0
2000	218.4	224.0	...
2048	...	...	213.5

Table LXXIX.—Temperature Coefficients in Conductivity Units.

v.	0°–4°.6.	4°.6–16°.5.	16°.5–25°.	25°–35°.
2	2.17	2.66	2.56	2.86
8	2.88	3.26	3.28	3.63
16	3.11	3.50	3.58	3.88
64	3.52	4.02	4.12	4.51
256	3.83	4.36	4.49	4.97
512	3.87	4.45	4.51	5.07
1024	4.00	4.57	4.66	5.30
2048	4.02	4.63	4.80	5.34

Table LXXX.—Temperature Coefficients in Per Cent.

v.	0°–4°.6.	4°.6–16°.5.	16°.5–25°.	25°–35°.
2	2.51	2.75	2.00	1.91
8	2.91	2.90	2.17	2.02
16	2.96	2.93	2.22	2.03
64	3.03	3.04	2.29	2.10
256	3.06	3.06	2.30	2.13
512	3.06	3.08	2.29	2.19
1024	3.05	3.06	2.28	2.18
2048	3.03	3.06	2.33	2.16

Table LXXXI.—Percentage Dissociation.

v.	α 0°.	α 4°.6.	α 16°.5.	α 25°.	α 35°.
2	65.3	63.9	62.1	60.7	59.4
8	74.6	74.3	73.2	72.4	71.6
16	79.3	79.0	78.1	77.5	76.6
64	87.6	87.6	87.3	87.1	86.6
256	94.3	94.4	94.4	94.3	94.0
512	95.3	95.4	95.6	95.3	95.2
1024	98.6	98.7	98.8	98.5	98.6
2048	100.0	100.0	100.0	100.0	100.0

Magnesium Chloride.

The original solution was standardized gravimetrically, by determining the chlorine as silver chloride. As is shown by the tables, the effect of temperature on dissociation and on the temperature coefficient of conductivity, expressed in percentage of conductivity units, is of the same general nature as in the case of the other substances we have considered. In Tables LXXXII. and LXXXIII. the same temperature effect is likewise noticed.

Table LXXXII.—Molecular Conductivities.

v.	μ_v 0°.	μ_v 14°.9.	μ_v 25°.	μ_v 35°.
2	67.59	99.09	122.8	148.3
8	81.35	120.8	150.3	182.5
16	86.87	129.6	161.2	195.2
32	92.26	137.4	171.7	208.4
128	100.3	151.6	189.2	231.4
512	105.3	159.8	200.6	245.8
1024	106.9	162.5	203.2	249.1

Table LXXXIII.—Temperature Coefficients in Conductivity Units.

v.	0°-14°.9.	14°.9-25°.	25°-35°.
2	2.11	2.35	2.55
8	2.65	2.92	3.22
16	2.87	3.13	3.40
32	3.03	3.40	3.67
128	3.44	3.72	4.22
512	3.66	4.03	4.52
1024	3.73	4.03	4.59

Table LXXXIV.—Temperature Coefficients in Per Cent.

v.	0°-14°.9.	14°.9-25°.	25°-35°.
2	3.12	2.37	2.08
8	3.26	2.42	2.14
16	3.30	2.42	2.11
32	3.28	2.47	2.13
128	3.43	2.45	2.22
512	3.48	2.59	2.25
1024	3.49	2.48	2.26

Table LXXXV.—Percentage Dissociation.

v.	α 0°.	α 14°.9.	α 25°.	α 35°.
2	63.2	61.0	60.4	59.5
8	76.1	74.3	74.0	73.3
16	81.3	79.8	79.3	78.4
32	86.3	84.6	84.5	83.7
128	93.8	93.3	93.1	92.9
512	98.5	98.3	98.7	98.7
1024	100.0	100.0	100.0	100.0

Zinc Sulphate.

The specimen of salt used was dried for several days, in an air-bath, at 110°. This was found necessary to bring it to constant weight. It was preserved in a desiccator until required. In Table LXXXVII. the comparison of our values of the molecular conductivities, with the results obtained experimentally by Kohlrausch, at 18°, shows a very close agreement. Conductivity measurements, in the case of this salt, were made at only 3 temperatures.

Table LXXXVI.—Molecular Conductivities.

v.	μ_v 0°.	μ_v 15°.	μ_v 25°.
2	30.57	45.56	56.62
8	43.20	64.74	80.01
16	50.99	75.20	93.6
32	59.37	86.96	108.8
128	76.61	115.8	144.8
512	97.0	147.3	185.1
1024	104.7	156.9	197.8
2048	113.3	170.4	213.0
8192	117.0	176.0	218.0

Table LXXXVII.—Comparison with the Work of Kohlrausch.

	Kohlrausch.	Calculated.
v.	μ_v 18°.	μ_v 18°.
2	49.8	48.89
4	60.4	. .
8	. .	69.33
16	. .	80.72
20	86.2	. .
1000	172.2	. .
1024	. .	169.14
2000	183.8	. .
2048	. .	183.3

Table LXXXVIII.—Temperature Coefficients in Conductivity Units.

v.	0°.15.	15°–25°.
2	0.999	1.11
8	1.44	1.53
16	1.61	1.84
32	1.84	2.18
128	2.61	2.90
512	3.36	3.78
1024	3.48	4.09
2048	3.80	4.26
8192	3.93	4.20

Table LXXXIX.—Temperature Coefficients in Per Cent.

v.	0°.15.	15°–25°.
2	3.27	2.44
8	3.33	2.36
16	3.16	2.45
32	3.10	2.51
128	3.41	2.50
512	3.46	2.57
1024	3.32	2.61
2048	3.35	2.50
8192	3.36	2.39

Table XC.—Percentage Dissociation.

v.	α 0°.	α 15°.	α 25°.
2	26.1	25.9	25.9
8	36.9	36.8	36.7
16	43.6	42.7	42.9
32	50.7	49.4	49.9
128	65.5	65.8	66.4
512	82.9	83.7	84.9
1024	89.5	89.2	90.7
2048	96.8	96.8	97.7
8192	100.0	100.0	100.0

Manganese Chloride.

The strength of the solution of this salt was determined gravimetrically, the manganese being weighed as the oxide, Mn_4O_4.

Table XCI.—Molecular Conductivities.

v.	μ_v 0°.	μ_v 10°.4.	μ_v 25°.	μ_v 35°.
2	68.14	89.64	121.3	145.0
8	84.98	113.5	156.7	188.1
16	91.79	121.9	169.0	205.1
32	97.4	130.0	181.6	221.2
128	107.0	143.8	202.5	246.7
512	114.1	154.0	216.6	264.5
1024	114.9	154.9	216.8	265.4

Table XCII.—Temperature Coefficients in Conductivity Units.

v.	0°-10°.4.	10°.4-25°.	25°-35°.
2	2.07	2.17	2.37
8	2.74	2.96	3.14
16	2.89	3.23	3.61
32	3.13	3.53	3.96
128	3.54	4.02	4.42
512	3.83	4.28	4.79
1024	3.85	4.24	4.86

Table XCIII.—Temperature Coefficients in Per Cent.

v.	0°-10°.4.	10°.4-25°.	25°-35°.
2	3.03	2.42	1.95
8	3.22	2.61	2.00
16	3.15	2.65	2.14
32	3.21	2.72	2.13
128	3.31	2.79	2.18
512	3.37	2.80	2.22
1024	3.35	2.74	2.24

Table XCIV.—Percentage Dissociation.

v.	α 0°.	α 10°.4.	α 25°.	α 35°.
2	59.3	57.9	56.0	54.6
8	74.0	73.3	72.3	70.9
16	79.0	78.7	78.0	77.3
32	84.8	83.9	83.8	83.1
128	93.1	92.8	93.4	93.0
512	99.3	99.4	99.9	99.7
1024	100.0	100.0	100.0	100.0

Manganese Nitrate.

The strength of the mother-solution was determined gravimetrically, the manganese being weighed as the oxide, Mn_3O_4.

Table XCV.—Molecular Conductivities.

v.	μ_v 0°.	μ_v 10°.2.	μ_v 25°.	μ_v 35°.
2	66.1	85.4	116.3	138.7
8	83.1	104.1	144.3	172.5
16	85.5	111.5	154.5	185.1
32	90.5	118.8	165.0	197.9
128	98.3	129.7	182.0	219.8
512	104.8	138.4	194.6	236.2
1024	105.4	139.3	195.8	237.4

Table XCVI.—Temperature Coefficients in Conductivity Units.

v.	0°-10°.2.	10°.2-25°.	25°-35°.
2	1.89	2.09	2.24
8	2.06	2.72	2.82
16	2.55	2.90	3.06
32	2.77	3.12	3.29
128	3.07	3.53	3.78
512	3.29	3.08	4.16
1024	3.33	3.82	4.16

Table XCVII.—Temperature Coefficients in Per Cent.

v.	0°-10°.2.	10°.2-25°.	25°-35°.
2	2.86	2.45	1.93
8	2.48	2.61	1.95
16	2.98	2.60	1.98
32	3.06	2.63	1.99
128	3.12	2.72	2.08
512	3.13	2.75	2.14
1024	3.15	2.74	2.13

Table XCVIII.—Percentage Dissociation.

v.	α 0°.	α 10°.2.	α 25°.	α 35°.
2	62.7	61.3	59.4	58.4
8	78.8	74.7	73.7	72.7
16	81.1	80.0	78.9	78.0
32	85.9	85.2	84.3	83.4
128	93.3	93.1	93.0	92.6
512	99.4	99.4	99.4	99.5
1024	100.0	100.0	100.0	100.0

Cobalt Chloride.

By means of several gravimetric determinations, as cobalt sulphate, the strength of the mother-solution was ascertained. From this the other solutions were obtained by dilution. It is apparent, from the tables, that results of the same character were obtained with cobalt chloride as with the other salts.

Hydrolysis probably came into play, to some extent, in the more dilute solutions.

Table XCIX.—Molecular Conductivities.

v.	μ_v 0°.	μ_v 7°.2.	μ_v 25°.	μ_v 35°.
2	71.77	87.16	129.5	154.9
8	87.75	107.4	161.5	195.4
16	94.08	115.3	174.2	211.3
32	100.2	122.8	186.7	226.6
128	109.6	135.1	207.1	252.1
512	116.5	143.7	221.2	270.5
1024	116.8	144.0	221.1	270.6

Table C.—Temperature Coefficients in Conductivity Units.

v.	0°-7°.2.	7°.2-25°.	25°-35°.
2	2.14	2.38	2.54
8	2.73	3.04	3.39
16	2.95	3.31	3.71
32	3.14	3.59	3.99
128	3.54	4.04	4.50
512	3.77	4.35	4.93
1024	3.78	4.33	4.95

Table CI.—Temperature Coefficients in Per Cent.

v.	0°-7°.2.	7°.2-25°.	25°-35°.
2	2.98	2.73	1.96
8	3.11	2.83	2.10
16	3.14	2.87	2.13
32	3.13	2.92	2.14
128	3.23	2.99	2.17
512	3.23	3.03	2.22
1024	3.24	3.01	2.24

Table CII.—Percentage Dissociation.

v.	α 0°.	α 7°.2.	α 25°.	α 35°.
2	61.4	60.5	58.6	57.2
8	75.1	74.6	73.0	72.2
16	80.5	80.1	78.8	78.1
32	85.8	85.3	84.4	83.7
128	93.8	93.8	93.7	93.2
512	99.7	99.8	100.0	100.0
1024	100.0	100.0	100.0	100.0

Cobalt Nitrate.

The strength of the original solution was determined gravimetrically, the cobalt being weighed as sulphate.

The salt is probably hydrolyzed, to some extent, in very dilute solutions.

Table CIII.—Molecular Conductivities.

v.	μ_v 0°.	μ_v 5°.4.	μ_v 25°.	μ_v 35°.
2	71.65	82.27	125.9	150.7
8	87.07	101.0	157.9	189.9
16	93.16	108.2	169.2	204.7
32	98.9	114.7	180.8	218.6
128	108.0	125.8	200.4	242.2
512	115.9	135.5	215.5	262.1
1024	116.1	135.4	215.3	262.0

Table CIV.—Temperature Coefficients in Conductivity Units.

v.	0°-5°.4.	5°.4-25°.	25°-35°.
2	1.97	2.23	2.48
8	2.39	2.90	3.20
16	2.79	3.11	3.55
32	2.92	3.37	3.78
128	3.30	3.81	4.18
512	3.63	4.08	4.66
1024	3.57	4.08	4.67

Table CV.—Temperature Coefficients in Per Cent.

v.	0°-5°.4.	5°.4-25°.	25°-35°.
2	2.75	2.71	1.97
8	2.74	2.87	2.03
16	2.99	2.87	2.09
32	2.95	2.94	2.09
128	3.06	3.03	2.09
512	3.13	3.01	2.16
1024	3.08	3.01	2.17

Table CVI.—Percentage Dissociation.

v.	α 0°.	α 5°.4.	α 25°.	α 35°.
2	61.7	60.8	58.5	57.5
8	75.0	74.6	73.3	72.5
16	80.2	79.9	78.6	78.1
32	85.2	84.7	84.0	83.4
128	93.0	92.9	93.1	92.4
512	99.8	100.0	100.0	100.0
1024	100.0	100.0	100.0	100.0

Nickel Chloride.

The original solution of nickel chloride was standardized electrolytically, according to the method of Smith and Exner. The salt was converted into sulphate, evaporated to dryness, the residue dissolved in ammonium sulphate and the solution treated with ammonia until strongly alkaline. The nickel was then determined electrolytically.

The salts of nickel, like those of cobalt, probably show small hydrolysis at high dilutions.

Table CVII.—Molecular Conductivities.

v.	μ_v 0°.	μ_v 6°.3.	μ_v 25°.	μ_v 35°.
2	73.07	86.49	131.7	158.0
8	89.51	106.3	164.8	198.9
16	95.79	114.4	177.4	215.3
32	102.1	122.0	190.5	231.2
128	112.0	134.7	211.6	256.8
512	119.9	144.5	227.2	276.8
1024	120.7	145.4	229.0	279.4

Table CVIII.—Temperature Coefficients in Conductivity Units.

v.	0°-6°.3.	6°.3-25°.	25°-35°.
2	2.13	2.42	2.63
8	2.67	3.13	3.41
16	2.95	3.37	3.79
32	3.16	3.66	4.07
128	3.57	4.11	4.52
512	3.90	4.42	4.96
1024	3.92	4.47	5.04

Table CIX.—Temperature Coefficients in Per Cent.

v.	0°-6°.3.	6°.3-25°.	25°-35°.
2	2.91	2.80	2.00
8	2.98	2.94	2.07
16	3.08	2.95	2.14
32	3.10	3.00	2.14
128	3.19	3.05	2.14
512	3.25	3.06	2.18
1024	3.25	3.07	2.20

Table CX.—Percentage Dissociation.

v.	α 0°.	α 6°.3.	α 25°.	α 35°.
2	60.5	59.5	57.5	56.6
8	74.2	73.1	72.0	71.2
16	79.4	78.7	77.5	77.1
32	84.6	83.9	83.1	82.7
128	92.8	92.6	92.4	91.9
512	99.3	99.4	99.2	99.1
1024	100.0	100.0	100.0	100.0

Nickel Nitrate.

The standardization of the mother-solution of nickel nitrate was carried out in the same manner as in the case of nickel chloride. The nickel was determined electrolytically, according to the method of Smith and Exner.

Table CXI.—Molecular Conductivities.

v.	μ_v 0°.	μ_v 6°.	μ_v 25°.	μ_v 35°.
2	71.34	83.06	125.3	150.4
8	87.35	102.7	157.9	190.0
16	93.67	109.9	169.7	204.8
32	99.15	116.8	180.9	218.6
128	108.3	128.7	200.1	242.9
512	116.1	137.2	215.4	261.3
1024	115.8	137.4	214.3	260.1

Table CXII.—Temperature Coefficients in Conductivity Units.

v.	0°-6°.	6°-25°.	25°-35°.
2	1.95	2.22	2.51
8	2.56	2.91	3.21
16	2.71	3.15	3.51
32	2.94	3.37	3.77
128	3.40	3.76	4.28
512	3.52	4.12	4.59
1024	3.60	4.05	4.58

Table CXIII.—Temperature Coefficients in Per Cent.

v.	0°-6°.	6°-25°.	25°-35°.
2	2.73	2.67	2.00
8	2.93	2.83	2.03
16	2.89	2.87	2.07
32	2.97	2.89	2.08
128	3.14	2.92	2.14
512	3.03	3.00	2.13
1024	3.11	2.95	2.14

Table CXIV.—Percentage Dissociation.

v.	α 0°.	α 6°.	α 25°.	α 35°.
2	61.6	60.5	58.5	57.8
8	75.4	74.7	73.7	73.0
16	80.9	80.0	79.2	78.7
32	85.6	85.0	84.4	84.0
128	93.5	93.7	93.4	93.4
512	100.0	99.9	100.0	100.0
1024	100.0	100.0	100.0	100.0

Copper Chloride.

The exact strength of the mother-solution was obtained by several gravimetric determinations. The copper was precipitated with sodium hydroxide and weighed as cupric oxide. The solution was then diluted to 0.5 N and from this the others were obtained by dilution.

Hydrolysis comes into play here to a greater extent than with any of the previous salts. This is shown in the conductivities, which continue to increase even at the highest dilutions studied. We think that the value of μ_v at 1000 liters is not widely removed from the true value of μ_∞.

Table CXV.—Molecular Conductivities.

v.	μ_v 0°.	μ_v 13°.8.	μ_v 25°.	μ_v 35°.
2	68.95	96.36	119.8	141.3
8	87.57	127.0	158.3	189.9
16	94.82	137.0	173.5	208.6
32	101.3	147.1	187.5	226.2
128	111.5	164.5	210.1	255.6
512	118.4	175.3	224.0	273.4
1024	123.0	181.7	232.2	282.6

Table CXVI.—Temperature Coefficients in Conductivity Units.

v.	0°-13°.8.	13°.8-25°.	25°-35°.
2	1.99	2.09	2.15
8	2.86	2.79	3.16
16	3.06	3.26	3.51
32	3.32	3.61	3.87
128	3.84	4.07	4.55
512	4.12	4.35	4.94
1024	4.25	4.51	5.04

Table CXVII.—Temperature Coefficients in Per Cent.

v.	0°-13°.8.	13°.8-25°.	25°-35°.
2	2.89	2.17	1.79
8	3.26	2.20	2.00
16	3.23	2.37	2.02
32	3.28	2.45	2.06
128	3.44	2.47	2.17
512	3.48	2.48	2.20
1024	3.46	2.48	2.17

Table CXVIII.—Percentage Dissociation.

v.	α 0°.	α 13°.8.	α 25°.	α 35°.
2	56.1	53.0	51.6	50.0
8	71.2	69.9	68.2	67.2
16	77.1	75.4	74.7	73.8
32	82.4	81.0	80.7	80.0
128	90.7	90.5	90.5	90.4
512	96.3	96.5	96.5	96.7
1024	100.0	100.0	100.0	100.0

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Copper Nitrate.

The solution of this salt was standardized gravimetrically, the copper being weighed as cupric oxide. Conductivity measurements were made at 5 different temperatures. The effect of temperature on conductivity, temperature coefficients and dissociation is the same as with the other salts we have considered.

The remarks in reference to hydrolysis apply here, as in the case of copper chloride.

Table CXIX.—Molecular Conductivities.

v.	μ_v 0°.	μ_v 5°.	μ_v 15°.8.	μ_v 25°.	μ_v 35°.
2	69.38	79.17	102.5	123.3	147.1
8	86.48	99.21	130.0	156.7	188.5
16	93.0	106.7	140.2	169.4	204.0
32	99.15	113.8	150.0	181.8	219.9
128	109.0	125.5	166.5	201.9	245.0
512	117.7	136.1	180.2	218.4	266.6
1024	119.8	138.6	183.3	222.9	271.7

Table CXX.—Temperature Coefficients in Conductivity Units.

v.	0°-5°.	5°-15°.8.	15°.8-25°.	25°-35°.
2	1.96	2.16	2.26	2.38
8	2.55	2.85	2.90	3.18
16	2.74	3.10	3.17	3.46
32	2.93	3.35	3.46	3.81
128	3.30	3.80	3.85	4.31
512	3.68	4.08	4.15	4.82
1024	3.76	4.14	4.30	4.88

Table CXXI.—Temperature Coefficients in Per Cent.

v.	0°-5°.	5°-15°.8.	15°.8-25°.	25°-35°.
2	2.83	2.73	2.20	1.93
8	2.95	2.87	2.23	2.03
16	2.95	2.91	2.26	2.04
32	2.95	2.94	2.31	2.10
128	3.03	3.03	2.33	2.14
512	3.13	3.00	2.30	2.21
1024	3.14	2.99	2.35	2.19

Table CXXII—Percentage Dissociation.

v.	α 0°.	α 5°.	α 15°.8.	α 25°.	α 35°.
2	57.9	57.1	55.9	55.3	54.1
8	72.2	71.6	70.9	70.3	69.4
16	77.6	77.0	76.5	76.0	75.1
32	82.8	82.1	81.9	81.6	80.9
128	91.0	90.5	90.8	90.6	90.2
512	98.2	98.2	98.3	98.0	98.0
1024	100.0	100.0	100.0	100.0	100.0

Hydrochloric Acid.

The original solution was prepared by dissolving pure hydrochloric acid in redistilled water. By means of the hydrometer the solution was diluted to approximately 0.25 N concentration. The exact strength was then determined by diluting the original solution five times and titrating successive portions by means of a standard solution of potassium hydroxide. The potassium hydroxide solution used had been carefully standardized against sulphuric acid, which, in turn, had been standardized gravimetrically by precipitation as barium sulphate. From the data thus obtained, the mother-solution was diluted with the proper volume of water to make it exactly 0.25 N. This dilution was then checked by titrating. The other solutions were obtained by diluting the original one.

Hydrochloric acid is a very strong acid. This is shown by the fact that a 0.25 N solution is dissociated more than 90 per cent and the value of $\mu\infty$ is obtained at a volume of about 128. Table CXXIV. shows a close agreement between the values of

the molecular conductivities as found by Ostwald and Krannhals and those which we have obtained.

In Table CXXV., *the temperature coefficients in conductivity units decrease with rise in temperature.* This is true, in general, in the case of acids, while with salts the opposite is true. The effect of temperature on conductivity, percentage temperature coefficients of conductivity and dissociation is of the same general character as in the case of salts.

The temperature coefficients, in conductivity units, are very high and also the conductivities. This is due to the acid being one of the very strongest and the hydrogen ion being the swiftest of all ions.

Table CXXIII.—Molecular Conductivities.

v.	μ_v 0°.	μ_v 12°.5.	μ_v 25°.	μ_v 25°.
4	223.3	285.9	348.2	397.9
8	227.0	292.2	357.0	407.1
16	231.8	298.7	365.2	415.5
32	235.0	303.3	370.7	423.4
128	238.8	309.0	379.3	433.3
512	235.5	304.2	374.7	428.3
1024	221.5	287.7	353.4	405.3

Table CXXIV.—Comparison with the Work of Others.

	Ostwald.	Krannhals.	Calculated.
v.	μ_v 25°.	μ_v 18°.	μ_v 18°.
4	343	313	313.3
8	355	323	320.7
16	362	329	328.0
32	369	335	333.0
128	376	341	340.0

Table CXXV.—Temperature Coefficients in Conductivity Units.

v.	0°-12°.5.	12°.5-25°.	25°-35°.
4	5.01	4.98	4.97
8	5.22	5.18	5.01
16	5.35	5.32	5.03
32	5.46	5.39	5.27
128	5.62	5.62	5.40
512	5.50	5.64	5.36
1024	5.30	5.26	5.19

Table CXXVI.—Temperature Coefficients in Per Cent.

v.	0°-12°.5.	12°.5-25°.	25°-35°.
4	2.24	1.74	1.43
8	2.30	1.77	1.40
16	2.31	1.78	1.38
32	2.37	1.77	1.42
128	2.35	1.82	1.42
512	2.34	1.85	1.43
1024	2.39	1.83	1.47

Table CXXVII.—Percentage Dissociation.

v.	α 0°.	α 12°.5.	α 25°.	α 35°.
4	93.5	92.5	91.8	91.8
8	95.1	94.6	94.1	93.9
16	97.1	96.7	96.3	95.9
32	98.4	98.2	97.7	97.7
128	100.0	100.0	100.0	100.0

Nitric Acid.

The solution was prepared and standardized in the same manner as that of hydrochloric acid.

Results of the same general character were obtained with nitric acid as with hydrochloric acid. In Table CXXIX., the temperature coefficients, expressed in conductivity units, decrease with rise in temperature. Like hydrochloric acid, nitric acid is also a very strong electrolyte. The value of $\mu\infty$ is obtained at a value of about 128.

The same remarks apply to the temperature coefficients and the conductivity of nitric as to those of hydrochloric acid.

Table CXXVIII.—Molecular Conductivities.

v.	μ_v 0°.	μ_v 12°.5.	μ_v 25°.	μ_v 35°.
4	222.4	284.3	344.4	390.8
8	226.9	290.5	354.4	402.7
16	231.3	296.3	362.0	411.8
32	235.4	301.7	368.7	418.6
128	238.3	308.2	376.6	429.4
512	236.7	306.0	373.9	426.9
1024	231.4	299.9	366.5	419.8

Table CXXIX.—Temperature Coefficients in Conductivity Units.

v.	0°-12°.5.	12°.5-25°.	25°-35°.
4	4.95	4.81	4.64
8	5.09	5.11	4.83
16	5.20	5.25	4.98
32	5.30	5.36	4.99
128	5.59	5.47	5.28
512	5.54	5.43	5.30
1024	5.48	5.33	5.33

Table CXXX.—Temperature Coefficients in Per Cent.

v.	0°-12°.5.	12°.5-25°.	25°-35°.
4	2.23	1.69	1.35
8	2.24	1.76	1.36
16	2.25	1.77	1.38
32	2.25	1.78	1.35
128	2.34	1.77	1.40
512	2.34	1.77	1.42
1024	2.37	1.78	1.45

Table CXXXI.—Percentage Dissociation.

v.	α 0°.	α 12°.5.	α 25°.	α 35°.
4	93.3	92.2	91.4	91.0
8	95.2	94.3	94.1	93.8
16	97.1	96.1	96.1	95.9
32	98.8	97.9	97.6	97.5
128	100.0	100.0	100.0	100.0

Sulphuric Acid.

By means of the hydrometer and Lunge's tables, a solution approximately 0.25 N was made. A portion of this was then diluted ten times and this diluted portion standardized by precipitation with barium chloride. From the data thus obtained, the mother-solution was diluted to exactly 0.25 N. This dilution was then checked by further precipitation. The comparisons, given in Table CXXXIII., between our calculated results and those obtained experimentally by Kohlrausch at 18°, are not quite as satisfactory as the comparisons with other substances.

Table CXXXII.—Molecular Conductivities.

v.	μ_v 0°.	μ_v 16°.3.	μ_v 25°.	μ_v 35°.
4	292.9	382.8	419.3	457.2
8	303.9	393.9	431.5	471.7
16	323.6	417.3	456.6	498.0
32	347.2	450.0	491.4	533.6
128	403.6	535.6	589.4	646.2
512	442.7	601.1	675.2	753.0
2048	449.2	622.4	709.9	814.4
8192	441.6	618.2	708.6	816.3

Table CXXXIII.—Comparison with the Work of Kohlrausch.

	Kohlrausch.	Calculated.
v.	μ_v 18°.	μ_v 18°.
4	379.8	389.9
16	...	425.0
20	416.8	...
32	...	458.1
40	468.6	...
128	...	546.1
200	571.0	...
333	600.2	...
512	...	615.6
2000	663.2	...
2048	...	639.5

Table CXXXIV.—Temperature Coefficients in Conductivity Units.

v.	0°-16°.3.	16°.3-25°.	25°-35°.
4	5.52	4.20	3.79
8	5.52	4.32	4.02
16	5.75	4.52	4.14
32	6.31	4.76	4.22
128	8.10	6.18	5.68
512	9.72	8.52	7.78
2048	10.63	10.06	10.45
8192	10.83	10.39	10.77

Table CXXXV.—Temperature Coefficients in Per Cent.

v.	0°-16°.3.	16°.3-25°.	25°-35°.
4	1.88	1.10	0.90
8	1.49	1.10	0.93
16	1.78	1.08	0.91
32	1.82	1.06	0.86
128	2.01	1.15	0.96
512	2.19	1.42	1.15
2048	2.37	1.62	1.47
8192	2.45	1.68	1.52

Table CXXXVI.—Percentage Dissociation.

v.	α 0°.	α 16°.3.	α 25°.	α 35°.
4	65.2	61.5	59.1	56.1
8	67.7	63.3	60.8	57.9
16	72.0	67.0	64.3	61.2
32	77.3	72.3	69.2	65.5
128	89.8	86.1	83.0	79.3
512	98.6	96.6	95.1	92.5
2048	100.0	100.0	100.0	100.0

Oxalic Acid.

The sample of oxalic acid used was purified by repeated crystallizations and was then thoroughly air-dried. The mother-solution was made up by direct weighing, the others being obtained by dilution. As is shown by the values of the molecular conductivities given in Table CXXXVII., oxalic acid is much weaker than the other acids we have considered. With it, as with other acids and salts which we have studied, the effect of rise in temperature from 0° to 35° is to decrease the percentage temperature coefficients of conductivity.

Table CXXXVII.—Molecular Conductivities.

v.	μ_v 0°.	μ_v 11°.8.	μ_v 25°.	μ_v 35°.
2	79.43	100.1	123.1	135.6
8	123.5	156.3	189.8	212.3
16	147.2	186.4	227.1	255.2
32	169.8	215.1	262.3	295.8
128	203.8	260.2	318.9	361.1
512	223.7	285.3	349.9	397.1
2048	240.2	307.4	375.6	428.1
8192	265.0	334.0	412.0	466.0

Table CXXXVIII.—Temperature Coefficients in Conductivity Units.

v.	0°-11°.8.	11°.8-25°.	25°-35°.
2	1.75	1.74	1.25
8	2.77	2.54	2.25
16	3.32	3.08	2.81
32	3.84	3.58	3.35
128	4.78	4.45	4.22
512	5.22	4.89	4.72
2048	5.69	5.17	5.25
8192	5.85	5.91	5.40

Table CXXXIX.—Temperature Coefficients in Per Cent.

v.	0°-11°.8.	11°.8-25°.	25°-35°.
2	2.20	1.74	1.02
8	2.24	1.63	1.19
16	2.26	1.65	1.24
32	2.26	1.67	1.28
128	2.35	1.71	1.32
512	2.33	1.71	1.35
2048	2.36	1.68	1.40
8192	2.21	1.77	1.31

Discussion of Results.

It was pointed out in the historical review of this subject, that up to the present no final conclusions had been reached as to the exact effect of temperature on dissociation, over the range of temperature from 0° to 35°. A number of investigators have made conductivity measurements at different temperatures, but concordant results have not been obtained by those who have worked in this field. Moreover, no one has studied the exact temperature effect for any very large number of substances having different degrees of dissociation.

We have studied, in all, 32 substances, inorganic and organic, with very different degrees of dissociation. Without a single exception, results of the same character have been obtained with every one of them. The percentage dissociation and the percentage temperature coefficients of conductivity decrease with rise in temperature. The effect of temperature on

the temperature coefficients of conductivity, expressed in conductivity units, is, however, different in the case of salts from that in the case of acids. This fact has been clearly demonstrated. With salts, the temperature coefficients of conductivity, expressed in conductivity units, increase with rise in temperature, while, in the case of acids, they decrease with rise in temperature.

A number of tables have been incorporated, showing a comparison of our results with those of others. As we have seen, the agreement between the two sets of values has been, in general, satisfactory.

Sufficient evidence has, undoubtedly, been obtained in this investigation to justify the conclusion that the percentage dissociation and the percentage temperature coefficients of conductivity decrease with rise in temperature, from 0° to 35°.

From the data presented, it is apparent that the tables representing the percentage temperature coefficients of conductivity and percentage dissociation run parallel. The percentage temperature coefficients of conductivity and the percentage dissociation decrease with rise in temperature. These facts are interesting in the light of certain hypotheses, which have been advanced in recent years.

Dutoit and Aston[1] have suggested the following relation; that only in those solvents which are polymerized or associated, do dissolved substances conduct the current. That is, the more associated a solvent the greater its dissociating power. Dutoit and Friderich[2] have also shown this relation to be true in a number of cases.

Ramsay and Shields[3] proved that in many liquids the molecules are not the simplest possible, but are aggregates of these simplest molecules, having various degrees of complexity; that is, the liquid molecules are polymerized aggregates of the simplest molecules. Water, one of the strongest dissociants, has a high degree of association. At 0° the molecule is $(H_2O)_4$. As the temperature is raised, the association becomes less, as Ramsay and Shields showed by the following data:

[1] Compt. rend., **125**, 540 (1897).
[2] Bull. Soc. Chim., [3], **19**, 321 (1898).
[3] J. Chem. Soc., **63**, 1089 (1893).

	0°.	10°.	20°.	30°.	40°.
Association factor x	4	3.81	3.68	3.44	3.18

It is obvious that, as the temperature of an aqueous solution of an electrolyte is increased, the ionic mobility is increased. At the same time the solvent water is becoming less and less associated with rise in temperature. As the association of the solvent decreases its dissociating power becomes less, according to the hypothesis of Dutoit and Aston. Thus we have two conditions affecting conductivity with rise in temperature, and they work counter to each other. The ions move faster with rise in temperature, increasing the conductivity. The association of the solvent becomes less with rise in temperature and, consequently, its dissociating power becomes less. This diminishes the conductivity. These facts are brought out very clearly by the data presented.

We have seen that conductivity increases with rise in temperature, the percentage of increase in conductivity per degree, decreases with rise in temperature, and the dissociation decreases with rise in temperature. In brief, when the temperature of an aqueous solution of an electrolyte is raised, the association of the water is decreased. The effect of this is to diminish its dissociating power and this, in turn, decreases the dissociation of the dissolved substance. Dissociation, then, is driven back by rise in temperature. The conductivity of a solution is conditioned by the number of ions present and by their velocity. The effect of decrease in dissociation with rise in temperature is to reduce the amount of conducting substance, or the number of ions in the solution. Consequently, although conductivity increases with rise in temperature, due to increase in ionic mobility, the percentage of increase in conductivity, per degree, should decrease ; otherwise, the conductivity-temperature curve would not reach a maximum with rise in temperature. This fact is clearly brought out and is in harmony with previous work at high temperatures, which shows a maximum in the conductivity curve with rise in temperature. It is also in harmony with the idea advanced by Bousfield and Lowry, in their curve representing the effect of

temperature on the conductivity of a composite electrolyte. The curve reaches a maximum and then drops.

The results presented in these tables are interesting in connection with the hypothesis of Thompson and Nernst. J. J. Thompson[1] and, a little later, Nernst[2] pointed out that, if the forces which hold the atoms in the molecule are of an electrical nature, those solvents that have the highest dielectric constants should have the greatest dissociating power.

The work which has, thus far, been done shows that this is, in general, true.[3] O. U. Vonwiller[4] studied the dielectric constant of water, at various temperatures ranging from 0° to 28° and found that, with rise in temperature, the dielectric constant of water gradually decreased. If the dielectric constant of a solvent decreases with rise in temperature, then, according to the hypothesis of Thompson and Nernst, its dissociating power should decrease with rise in temperature. Consequently, the dissociation of the dissolved substance should decrease as the temperature rises. Fact and theory are in accord. We have shown that there is a decrease in dissociation with rise in temperature. The work of Vonwiller is, then, a connecting link between the Thompson-Nernst hypothesis and the experimental results obtained in this investigation. A number of electrolytes have been examined and, in each case, results of the same general character have been obtained.

It thus seems to be proved experimentally, for a large number of substances, what a few investigators have made probable for a few substances, over a wide range of temperature. Our results are in harmony with previous work at high temperatures, showing a maximum in the conductivity-temperature curve with rise in temperature, and also with the hypothesis of Bousfield and Lowry, in their curve representing the effect of temperature on the conductivity of a composite electrolyte. That there is a satisfactory agreement between the results of our experiments, the hypothesis of Dutoit and Aston and the work of Ramsay and Shields has been

[1] Phil. Mag., 36, 320 (1894).
[2] Z. physik. Chem., 13, 531 (1894).
[3] Jones and Carroll: This Journal, 32, 521 (1904).
[4] Phil. Mag., [6], 7, 655 (1904).

clearly demonstrated. We have also referred to the results of Vonwiller, and pointed out the fact that the Thompson-Nernst hypothesis holds admirably, in aqueous solutions, over a considerable range of temperature. When the temperature of an aqueous solution of an electrolyte is increased from 0° to 35°, the results expressed in tabular form are as follows:

With rise in temperature from 0° to 35°.	Association of solvent decreases.
	Dielectric constant of solvent decreases.
	Viscosity of solvent decreases.
	Dissociation of dissolved substance decreases.
	Percentage temperature coefficients of conductivity decrease.
	Ionic mobility increases.

SUMMARY AND CONCLUSIONS.

When the temperature of an aqueous solution of an electrolyte is raised from 0° to 35°, the effect of rise in temperature on conductivity, dissociation and on the temperature coefficient of conductivity has been determined and the following relation shown to exist:

Effect of Rise in Temperature from 0° to 35°.

1. A large increase in conductivity, due to increase in ionic mobility.

2. A small decrease in dissociation, in accordance with the law of Dutoit and Aston, connecting association of solvent and dissociation of dissolved substance, and in accordance with the results of Ramsay and Shields, showing a decrease in the association of water with rise in temperature.

3. From the results of Vonwiller, showing a decrease in the dielectric constant of water with rise in temperature, and the Thompson-Nernst hypothesis, connecting the dissociating power of a solvent with its dielectric constant, we should expect a decrease in dissociation with rise in temperature. This

has been demonstrated experimentally over a considerable range of temperature.

4. The temperature coefficients of conductivity, expressed in percentage of conductivity units, decrease with rise in temperature, and this fact is in accordance with the maximum in the conductivity-temperature curve of an electrolyte, as pointed out by Bousfield and Lowry, and with the work of former investigators at high temperatures.

5. The temperature coefficients of conductivity, expressed in conductivity units, in the case of salts increase with rise in temperature, while with acids they decrease with rise in temperature.

CHEMICAL LABORATORY,
JOHNS HOPKINS UNIVERSITY,
May, 1905.

Contributions from the Chemical Laboratory of Harvard College.

ON CERTAIN DERIVATIVES OF TETRABROMORTHOBENZOQUINONE.[1]

BY C. LORING JACKSON AND H. A. CARLTON.

In this paper we describe the continuation of the work on the action of alcohols on tetrabromorthobenzoquinone, $C_6Br_4O_2$, begun some years ago by Porter and one of us.[2]

When methyl alcohol is allowed to stand, at ordinary temperatures, with tetrabromorthoquinone, a red compound[3] is formed at first, which is later converted into the α-addition-compound, $(C_6Br_4O_2)_2.CH_3OH$. The nature of this red compound could not be established by analysis, because the differences in percentage composition between the most probable formulas fell well within the limits of experimental accuracy, we accordingly resorted to a series of synthetic experiments, which showed that it was formed by the union of 2 molecules of tetrabromorthoquinone with 1 of the α-body, its formula, therefore, is $(C_6Br_4O_2)_4.CH_3OH$, and it may be called the methyl alcohol tetrakis tetrabromorthobenzoquinone. We could not

[1] The work described in this paper formed part of a thesis presented to the Faculty of Arts and Sciences of Harvard University, for the degree of Doctor of Philosophy, by H. A. Carlton.

[2] THIS JOURNAL, 31, 89 (1904).

obtain a corresponding compound with benzyl alcohol, but from the phenomena observed in the action of ethyl alcohol on tetrabromorthoquinone we think it probable one is formed in that case.

When the red methyl alcohol compound, $(C_6Br_4O_2)_4.CH_3OH$, was warmed with a dilute solution of sodic hydrate, it was converted into the β-methyl alcohol compound, $(C_6Br_4O_2)_3.CH_3OH$. This observation led us to try the action of sodic hydrate on the α-bodies and we found that this reagent converted the methyl and benzyl compounds into the corresponding β-compounds, thus furnishing a good general method for making the β-compounds, which was much needed, as the only one known before (action of acetic anhydride) gave very impure products.

Experiments with ethyl alcohol, normal propyl alcohol and isoamyl alcohol resulted in the preparation of new α- and β-compounds. Tertiary butyl alcohol also seemed to give an α-compound, but our supply of the alcohol was not large enough to obtain it pure. In the following table the decomposition or melting-points of all the known bodies of these two classes are recorded. We have nothing to add to the statement of their general properties already given :[1]

	α.	β.
$(C_6Br_4O_2)_3.H_2O$	190°–200°	221°–222°
$(C_6Br_4O_2)_3.CH_3OH$	178°–182°	261°
$(C_6Br_4O_2)_3.C_2H_5OH$	180°–185°	228°
$(C_6Br_4O_2)_3.C_3H_7OH n$	180°	176°
$(C_6Br_4O_2)_3.C_5H_{11}OH i$	150°	177°
$(C_6Br_4O_2)_3.C_7H_7OH$	165°–170°	216°–217°

The α-isoamyl compound melts without reddening, but at a higher temperature (190°) it is converted into the red hexabromorthoquinopyrocatechin ether like the other α-bodies.

We have spent much time on the reduction of the α-bodies, as we hoped that this work might settle their constitution, but we found that the same product was formed from the water, methyl alcohol, or benzyl alcohol compounds, showing that the alcohol (or water) was split off and there also seemed to be a

[1] THIS JOURNAL, 31, 90 (1904).

deeper decomposition of the molecule, the fragments of which recombined to form the final product. We assign to this compound, melting at 274°–275°, the formula[1] $C_{18}Br_8O_6H_4$, which agrees with our analyses and with the discovery of a triacet derivative, melting at 273°–275° and a tribenzoyl derivative, melting at 250°–255°. Some unfinished experiments on the oxidation of the reduced substance showed that nitric acid converted it into a red product with essentially the same percentage of bromine, but treatment with chloroform separated this product into red prisms, melting at about 275°–280° and yellow needles not melting at 310°. The work must be repeated on a much larger scale to obtain enough of these bodies to determine their nature.

The formula $C_{18}Br_8O_6H_4$ can be developed into

$$C_6Br_4 : O_2 : C_6H(OH)_2\,O.C_6Br_4OH,$$

which explains all the observed facts, but much more experimental work is necessary before it can be considered established. For purposes of indexing it may be called, provisionally, *octobromdihydroxyhemipyrocatechinepyrocatechine ether.* Such a substance would be formed from compounds with either of the two formulas[2] assigned to the α-bodies by reactions which involve no very strained hypotheses, and are about equally probable, so that these experiments throw no light on the structure of the α-compounds.

Some experiments with the β-compounds established little beyond confirming the previous observation that they are very stable substances.

EXPERIMENTAL.

The tetrabromorthobenzoquinone used by us was prepared by the method of Zincke,[3] with the modifications described in other papers[4] from this laboratory. We have found, however,

[1] The percentage of bromine in this substance, 67.05, is so close to that in $(C_6Br_4O_2)_2H_4.C_7H_7OH$ (66.67) that Porter and one of us (THIS JOURNAL, 31, 105) assigned to it this incorrect formula.

[2] THIS JOURNAL, 31, 93 (1904).

[3] Ber. d. chem. Ges., 20, 177 (1887).

[4] Jackson and Koch: THIS JOURNAL, 26, 34 (1901). Jackson and Porter: *Ibid.*, 30, 522 (1903).

if the quinone, after its formation, is precipitated by the addition of 1200 cc. of water instead of 300 cc., that the yield is larger and there is no diminution in the purity of the product. The preparations used by us melted generally between 145°–147°, in some cases as high as 150°, instead of 150°–151°, but the loss in purification is so great that we did not attempt to recrystallize them and, as a matter of fact, such specimens proved to be quite pure enough for our work.

Red Compound of Tetrabromorthoquinone and Methyl Alcohol.

This substance was obtained by Porter and one of us[1] as the first product of the action of cold methyl alcohol on the orthoquinone, since it is usually formed after standing for 24 hours, but in that paper only analyses of the substance are given, which are not enough to establish its composition, as the differences between the percentages of the elements in the most probable formulas are nearly, if not quite, within the limits of experimental error. In taking up the subject again we tried to settle the composition of the substance by the following synthetic experiments:

In the first place it was found that the red compound could be formed by the action of tetrabromorthoquinone on the α-compound of tetrabromorthoquinone and methyl alcohol,[2] $(C_6Br_4O_2)_2.CH_3OH$ (formed by longer action of methyl alcohol on the quinone). Accordingly:

(1) Five tenths gram of the α-body were mixed with 0.24 gram of tetrabromorthoquinone dissolved in 5 cc. of benzene, giving the proportion of 1 molecule of the quinone to each molecule of the α-body. The greater part of the α-body remained undissolved in the bottom of the flask, but after standing over night it was found that small, dark-red prisms had begun to crystallize out of the benzene and that the white α-compound was partially converted into a red substance. After 24 hours the reaction seemed to be complete, as no more of the white substance was converted into the red, but for greater certainty the mixture was allowed to stand for 2 more

[1] THIS JOURNAL, 31, 96 (1904).
[2] *Ibid.*, 31, 97 (1904).

days. The benzene was then poured off, mixed with a little ligroin and allowed to evaporate spontaneously. In this way small, dark-red crystals were obtained, which were recognized by their melting-point, 194°–195°, and crystalline form as the red methyl alcohol compound. The residue in the flask consisted of the red substance and the α-body, showing that more than 1 molecule of the quinone was needed to convert the α-compound into the red body.

(2) Five-tenths gram of the α-body were mixed with a solution of 0.48 gram tetrabromorthoquinone in 5 cc. of benzene, that is, 2 molecules of the quinone for each molecule of the α-body. The experiment ran as in (1) except that all the α-compound was converted into the red crystals melting at 194°–195° and the benzene solution, when allowed to evaporate with a little ligroin, gave only these crystals with a small amount of a red tar around the edges, no α-body or quinone being visible.

(3) Five-tenths gram of the α-body were mixed with 0.72 gram of tetrabromorthoquinone, that is, 3 molecules of the quinone to each molecule of the other component. The reaction in this experiment ran much more rapidly than in the other two, as the red compound began to crystallize out in half an hour. Finally all the white α-body was converted into the red product and the benzene, when mixed with ligroin and allowed to evaporate, yielded a mixture of the red prisms of the methyl alcohol body and the long red needles of tetrabromorthoquinone.

It is evident, from these experiments, that the red compound is formed by the union of 2 molecules of tetrabromorthoquinone with 1 of the α-body, $(C_6Br_4O_2)_2.CH_3OH$. This result is in harmony with the analyses, as shown by the following table, in which the results obtained by Porter[1] and an analysis of the product of Experiment 2 are compared with those calculated for the formula established by the syntheses.

0.1885 gram substance gave, by the Carius method, 0.3280 gram AgBr.

[1] This JOURNAL, 31, 96 (1904).

	Calculated for $(C_6Br_4O_2)_4.CH_3OH$.	Found. Porter.		Carlton.
C	17.36	17.48		. .
H	0.23	0.66		. .
Br	74.08	73.83	73.90	74.03

Properties of the Red Compound, Methylalcoholtetrakistetrabromorthobenzoquinone.—As observed by Porter, it crystallizes in small, transparent, well-formed prisms of a cherry-red color, which are soluble in alcohol or benzene. Benzene mixed with ligroin is the best solvent for it. It usually crystallizes unaltered from this mixture, but occasionally it is decomposed partially under these conditions, yielding the α-body and tetrabromorthoquinone. Our observations on its behavior toward heat differ slightly from those of Porter, as we found it melts at 194°–195° instead of at 192°–193, and it is not stable at temperatures below its melting-point, as he states, but, if heated slowly, decomposes somewhat above 140°, forming a brick-red substance. Under these circumstances the difference of 2° between the earlier and later determinations of the melting-point is not surprising; in fact, the melting-point 194°–195° could be obtained only by dipping the tube into the hot bath, so as to make the heating as short as possible. When the red compound is allowed to stand in the cold with methyl alcohol, it gradually turns white and at the end of 2 weeks is completely converted into the α-compound of tetrabromorthoquinone and methyl alcohol. A dilute solution of sodic hydrate converts the red substance into a white body, as described later in this paper.

An attempt to prepare a substance similar to the red methyl compound just described from the α-benzyl alcohol tetrabromorthoquinone, $(C_6Br_4O_2)_3.C_7H_7OH$, gave a negative result. This α-body was mixed with a benzene solution of the quinone in the proportion of 2 molecules of the latter to each molecule of the former, but after standing a week the white α-benzyl compound remained unchanged on the bottom of the flask.

Action of Sodic Hydrate on the Red Methyl Alcohol Compound.

When the methyl alcohol tetrakistetrabromorthoquinone,

$(C_6Br_4O_2)_4.CH_3OH$,

was treated with a dilute solution of sodic hydrate, it was gradually converted into a white product and the alkaline solution assumed a dark, brownish-yellow color. After heating on the water-bath for an hour the liquid was poured off and was found to give a test for bromine with chlorine water and chloroform. The white solid product was washed three times with hot water by decantation, when it was found to turn dark at 200° and melt at 245°. On crystallization from benzene white crystals were obtained, which melted at 259°–260° and agreed in their other properties with the β-methyl alcohol compound, $(C_6Br_4O_2)_2.CH_3OH$. The red compound, therefore, is converted into the β-compound by hot sodic hydrate, in aqueous solution.

Action of Sodic Hydrate on Orthoquinone Addition Compounds of the Alpha Series.

As the work described in the preceding paragraph showed that sodic hydrate converted the red methyl compound into the β-methyl compound, it occurred to us that it might have a similar effect on the α-compounds, and the following experiments show that this is the case; we have, therefore, in the action of sodic hydrate, a good general method for converting α- into β-compounds, which was much needed.

Sodic Hydrate and the α-Benzyl Alcohol Compound.—One gram of the α-compound, $(C_6Br_4O_2)_2.C_7H_7OH$, was heated on the steam-bath with dilute sodic hydrate, for 1 hour. At the end of this time the orange-red solution was poured off from the white, insoluble portion. This liquid smelled of benzyl alcohol, but gave no test for bromine with chlorine water and chloroform. The solid was washed three times by decantation with hot water and melted, in this crude state, at 200°–210°, but recrystallization from a mixture of benzene and ligroin soon raised it to the constant melting-point 218°–219°. The melting-point of the β-benzyl alcohol compound was determined by Porter and one of us[1] as 216°–217°, but as our product shows all the properties of the β-compound, we ascribe this

[1] This Journal, 31, 104 (1904).

difference in the melting-point to the greater purity of our preparation, since the acetic anhydride method of making the β-compound—the only one known to Porter—gives a very impure product, which it is hard to purify thoroughly. For greater safety our product was dried at 100° and analyzed with the following result:

0.1659 gram substance gave 0.2613 gram AgBr.

	Calculated for $(C_6Br_4O_2)_2.C_7H_7OH$.	Found.
Br	66.95	67.01

Sodic Hydrate and the α-Methyl Alcohol Compound.—The α-methyl alcohol compound, $(C_6Br_4O_2)_2.CH_3OH$, after it had been heated with dilute sodic hydrate, on the steam-bath, for an hour, was converted into a pure white substance which, after recrystallization from benzene, showed the constant melting-point 259°–261° and was also identified with the β-compound by its other properties.[1]

Action of Other Alcohols on Tetrabromorthobenzoquinone.

The object of this work was to determine whether other alcohols formed α- and β-compounds with tetrabromorthoquinone similar to those obtained with methyl alcohol and with benzyl alcohol.

α-Compound from Ethyl Alcohol, $(C_6Br_4O_2)_2.C_2H_5OH$.—Five grams of tetrabromorthoquinone were mixed thoroughly with 10 cc. of absolute alcohol and the mixture allowed to stand in a corked flask, at ordinary temperatures. After 1 day there appeared a mass of orange crystals mixed with a few that were white. At the end of a week the liquid had become green and the white substance had disappeared entirely, but after 2 weeks there was a new deposit of white crystals. The mixture was allowed to stand 1 week more (4 weeks in all) to secure the completion of the reaction, and the crystals were then filtered out, washed with alcohol, recrystallized from a mixture of 1 part of benzene with 2 of alcohol and then dried at 100° for analysis.

[1] The formation of the β-compounds, by the action of sodic hydrate, explains the behavior of the α-benzyl alcohol compound with sodium amalgam. THIS JOURNAL, 31, 106.

0.1639 gram substance gave, by the Carius method, 0.2772 gram AgBr.

	Calculated for $(C_6Br_4O_2)_2.C_2H_5OH$.	Found.
Br	71.60	71.96

That the substance belongs to the α-series is shown by its behavior when heated; at 150° it begins to redden and at 180°–185° melts to a bright red liquid, which is soon converted into a red solid. As this is a decomposition-point rather than a melting-point, a more definite temperature cannot be given.

Properties of the α-Ethyl Alcohol Tetrabromorthoquinone.—It crystallizes from benzene and alcohol in small, white, spherical bodies made up of very minute crystals. Its behavior with heat is described in the preceding paragraph. It is freely soluble in benzene, ether, chloroform, acetone, or carbonic disulphide; nearly insoluble in cold alcohol, but fairly soluble in it when hot; insoluble in cold ligroin or glacial acetic acid, slightly soluble in hot; essentially insoluble in water; unaffected by the three strong acids.

β-Ethyl Alcohol Tetrabromorthoquinone, $(C_6Br_4O_2)_2.C_2H_5OH$. —This compound could not be obtained from the α-body by boiling it with alcohol. In fact, so far as our experience goes, that method of converting an α- into a β-body applies only to the methyl compound. Accordingly, we obtained the β-compound by the sodic hydrate method described earlier in this paper. Two grams of the crude α-compound, made as just described, were heated on the steam-bath, for an hour, with a dilute solution of sodic hydrate. The resulting reddish-brown liquid was poured off and the white solid, after washing three times with hot water, was recrystallized from a mixture of 1 part of benzene with 2 of alcohol, until it showed the constant melting-point 228°, when it was dried at 100° and analyzed.

0.1672 gram substance gave 0.2819 gram AgBr.

	Calculated for $(C_6Br_4O_2)_2.C_2H_5OH$.	Found.
Br	71.60	71.74

Properties of the β-Ethyl Alcohol Tetrabromorthoquinone.—It crystallizes in small, white, rhombic plates and melts at 228° without darkening or other signs of decomposition. It is freely soluble in benzene, ether, chloroform, acetone, or carbonic disulphide; essentially insoluble in cold glacial acetic acid, soluble in it when hot; essentially insoluble in cold alcohol or ligroin, slightly soluble when hot; insoluble in water. It is not affected by the three strong acids whether cold or hot.

α-Normal Propyl Alcohol Tetrabromorthoquinone, $(C_6Br_4O_2)_2$. C_3H_7OH.—Five grams of the tetrabromorthoquinone were thoroughly mixed with 10 cc. of normal propyl alcohol and the mixture was allowed to stand, at ordinary temperatures, in a corked flask. After a few days small orange prisms appeared, and after 2 weeks the action seemed to be complete, but it was allowed to stand 2 weeks longer to make sure. The solid product consisted of orange prisms mixed with a few red crystals. It was washed with a mixture of 1 part of benzene with 2 of ligroin and then recrystallized from a mixture of equal parts of these two solvents, after which it was dried at 100° and analyzed.

0.1539 gram substance gave 0.2554 gram AgBr.

	Calculated for $(C_6Br_4O_2)_2.C_3H_7OH$.	Found.
Br	70.46	70.62

As it decomposed with reddening when heated, it belongs to the α-series. It crystallized in small, transparent prisms of a light-yellow color and resembles the α-ethyl body in its other properties. It begins to turn red at 150° and melts to a red liquid at 180°.

β-Normal Propyl Alcohol Tetrabromorthoquinone, $(C_6Br_4O_2)_2$. C_3H_7OH.—One and one-half grams of the α-compound were heated on the steam-bath, for 1 hour, with a dilute solution of sodic hydrate. The yellow, alkaline liquid was then poured off and the solid product purified in the same way as the ethyl compound. It melted constantly at 176° and was dried at 100° for analysis:

0.1535 gram substance gave 0.2546 gram AgBr.

	Calculated for $(C_6Br_4O_2)_2.C_5H_7OH$.	Found.
Br	70.46	70.57

It crystallizes in small, white, six-sided plates and melts at 176° to a light-yellow liquid. In its other properties it resembles the β-ethyl compound.

α-Isoamyl Alcohol Tetrabromorthoquinone, $(C_6Br_4O_2)_2.C_5H_{11}OH$.—Five grams of tetrabromorthoquinone were thoroughly mixed with 10 cc. of isoamyl alcohol and allowed to stand at ordinary temperatures, in a corked flask. After 1 day, long orange crystals appeared and after 2 weeks the quinone was, apparently, entirely converted into this substance, but it was allowed to stand another week to make sure that the reaction was complete. The product, consisting of orange prisms mixed with a small amount of a red substance, was filtered out, washed with a mixture of benzene and ligroin and crystallized from ligroin. In this way two sorts of crystals were obtained, transparent yellow prisms and opaque rosettes of a pale-yellow color. These prisms melted at 150° to a yellow liquid, which gradually turned red and solidified at about 190°. The rosettes melted at 105° to a yellow liquid, also turning red and solidifying at about 190°. The rosettes, which formed the larger part of the product, were separated mechanically and recrystallized from ligroin, the resulting crystals were almost entirely prisms melting at 150°, while the few rosettes obtained now melted also at 150°. The prisms were dried at 100° for analysis.

0.1587 gram substance gave 0.2548 gram AgBr.

	Calculated for $(C_6Br_4O_2)_2.C_5H_{11}OH$.	Found.
Br	68.34	68.29

The α-isoamyl compound crystallizes in bright-yellow prisms, but, as mentioned in the preceding paragraph, it also occurred in rosettes showing a different crystalline habit, perhaps a different crystalline form. It is possible, therefore, that it is dimorphous, but it seems more probable that the formation of the rosettes was due to a trace of some impurity, which modified the habit of the crystals. This view receives a cer-

tain amount of support from the fact that the crude product was converted by ethyl alcohol, either hot or cold, into the hexabromorthoquinopyrocatechine ether, $C_6Br_4O_2C_6Br_2O_2$, recognized by its bright-red color, insolubility in the common solvents, infusibility below 300°, and the characteristic red prisms, obtained on crystallizing it from nitrobenzene. After one crystallization from ligroin the crude product still showed this behavior with ethyl alcohol, but not after two crystallizations. It is possible that the impurity, which caused the formation of the ether, was also responsible for the appearance of the rosettes. Similar cases of the formation of the ether from crude products by the action of alcohol have been observed in this laboratory, especially in the product of the action of acetic acid on the tetrabromorthoquinone.

The α-isoamyl alcohol compound melts at 150°, giving a yellow liquid, and in this respect differs from the other compounds of the α-series, which turn red when they melt. This difference is, however, more apparent than real, since this substance, if heated to a higher temperature, turns red and at 190° is converted into a red solid. It is evident, therefore, that the melting-point of the isoamyl compound lies below the point of decomposition, whereas the higher melting-points of the other α-bodies known lie above this point. In solubilities the isoamyl body resembles the other α-compounds, except that it is more soluble than they are in ligroin, which is the best solvent for it.

β-Isoamyl Alcohol Tetrabromorthoquinone, $(C_6Br_4O_2)_2.C_5H_{11}OH$.—This substance was prepared by treating the α-compound with dilute sodic hydrate, as described under the other β-bodies. After recrystallization from benzene and alcohol it showed the constant melting-point 177°, when it was dried at 100° and analyzed.

0.1568 gram substance gave 0.2531 gram AgBr.

	Calculated for $(C_6Br_4O_2)_2.C_5H_{11}OH$.	Found.
Br	68.34	68.69

It crystallizes in small, white prisms melting at 177° and resembles the other β-compounds in solubility.

Action of Tertiary Butyl Alcohol on Tetrabromorthoquinone.

Five grams of tetrabromorthoquinone were mixed with 10 cc. of the alcohol and allowed to stand in a corked flask. The action was much slower than with the other alcohols studied, but after 3 days some small, white prisms appeared. As the alcohol usually solidified over night, it was necessary to warm the mixture to melt it, but even this did not make the reaction run so fast as in other cases. After 4 weeks the orange-red, crystalline product was washed with a mixture of 1 part of benzene to 2 of ligroin and then recrystallized from a mixture of equal parts of these solvents, but the product was not homogeneous, since it consisted of yellow needles and short, red prisms. Unfortunately, the amount of the tertiary alcohol at our disposal was too small to allow us to make a further study of this product.

Reduction of the α-Methyl Alcohol Compound, $(C_6Br_4O_2)_2.CH_3OH$.

Five grams of the substance, mixed with a large excess of granulated zinc and 50 cc. of 95 per cent acetic acid, were heated on the steam-bath until the reaction started, and then allowed to stand at ordinary temperatures. The liquid turned dark-brown and the undissolved α-compound took on a slightly reddish color. After about 5 minutes light-brown needles began to separate from the solution, but the reaction was not complete until the mixture had stood 4 or more days. The action ran much faster when the flask was heated, but as this gave a less pure product, we found it wiser to carry on the reduction in the cold. After the α-compound had disappeared, the brown needles were filtered out and washed first with dilute acetic acid, and afterward with warm water. The crude product, which melted at 265°–270°, was recrystallized from benzene until it showed the constant melting-point 274°–275°, when it was dried at 100° and analyzed:

I. 0.2227 gram substance gave, on combustion, 0.1853 gram CO_2 and 0.0113 gram H_2O.

II. 0.2552 gram substance gave 0.2142 gram CO_2 and 0.0133 gram H_2O.

III. 0.1665 gram substance gave, by the Carius method, 0.2630 gram AgBr.

IV. 0.1594 gram substance gave 0.2525 gram AgBr.

V. 0.2079 gram substance gave 0.3292 gram AgBr.

	Calculated for $C_{18}Br_8O_6H_4$.	Found. I.	II.	III.	IV.	V.
C	22.59	22.69	22.90	. .	. .	. .
H	0.42	0.57	0.58	. .	. .	. .
Br	66.94	. .	. .	67.22	67.41	67.38

Porter found 67.40 per cent of bromine in the product obtained by reducing the α-benzyl alcohol compound. The results obtained agree better with the formula $C_{18}Br_8O_6H_4$ than with that given, but as the study of the acet and benzoyl derivatives shows that it contains three hydroxyl groups, the formula with 4 atoms of hydrogen must be adopted.

The filtrate from this reduction-product had a beautiful purplish-red color, but we found the organic compound it contained very unmanageable, since, on spontaneous evaporation, it gave a tar (with which ferric chloride produced a dark-green solution, indicating the presence of a pyrocatechin), while the addition of a large quantity of water threw down a flocculent white precipitate, which gradually turned brown. In the filtrate from this we obtained a good test for a bromide with argentic nitrate and nitric acid.

Reduction of Other α-Bodies.

The reduced methyl compound described above resembles closely the reduction-product from the α-benzyl compound prepared by Porter and one of us,[1] which was described as having a pale straw color and melting at 273°–274°. To make sure they were identical, the reduction was repeated with 2 grams of the α-benzyl alcohol body, $(C_6Br_4O_2)_2.C_7H_7OH$, an excess of granulated zinc and 20 cc. of 95 per cent acetic acid. The reaction ran more slowly than with the methyl compound and it was found necessary to heat the mixture frequently in order to make the reduction complete. At the end of 6 days brown needles were obtained, which, after crystallization from ben-

[1] This Journal, 31, 105 (1904).

zene, showed the constant melting-point 274°–275°, and coincided in every respect with the product from the methyl alcohol body.

The α-water compound, $(C_6Br_4O_2)_2.H_2O$ (made by the action of ordinary toluene on tetrabromorthoquinone), was also reduced. The preparation of this water compound ran much more slowly than before, occupying 4 weeks instead of 1. This was probably due to the presence of less moisture than usual in the specimen of toluene used. When reduced as in the previous cases, the liquid became yellowish-brown and brown needles were deposited at once. The reaction seemed to be complete after standing for a few hours at ordinary temperatures (it was started by gentle heating), but the mixture was allowed to stand a day for greater certainty. This reduction, therefore, is much more rapid than that of the alcohol compounds. The product, after crystallization from benzene, melted constantly at 274°–275° and was identical with the others. The filtrate from the brown crystals was colorless, while the alcohol compounds gave a reddish-purple filtrate. It contained bromide.

The red methyl alcohol compound, $(C_6Br_4O_2)_4.CH_3OH$, when reduced with zinc and acetic acid, yielded the same product melting at 274°–275°. In this case the reduction seemed to be complete after 3 days, but the mixture was allowed to stand 4.

Properties of the Reduced α-Bodies. Octobromdihydroxyhemipyrocatechinepyrocatechine Ether.—It crystallizes from benzene in small, light-brown prisms with a characteristic silky luster, which unite to form large, compact leaves. It melts at 274°–275° and is insoluble in most of the organic solvents when cold, only slightly soluble in them when boiling. It is, however, fairly soluble in boiling benzene or acetone and readily soluble in boiling nitrobenzene. Hot sulphuric acid or hydrochloric acid has no action on it; nitric acid converts it into a red product melting at 295°, described later. Sodic hydrate turns it to a purple substance. Acetic anhydride and sodic acetate give acet compounds, described in the next section.

Action of Acetic Anhydride on the Octobrom Reduction-product.—One gram of the reduction-product, mixed with 1 gram of dry sodic acetate, was boiled with 20 cc. of acetic anhydride until it dissolved, which usually took about 5 minutes, and the product was then precipitated with water. The products from different preparations varied in melting-points from 265°–270° to 280°–285°, and from white to pale-brown in color. All of them together were recrystallized from a mixture of 2 parts of benzene with 1 of alcohol, until two different bodies were isolated, one of which melted constantly at 304°–305° and proved to be the diacet compound, the other, melting constantly at 273°–275°, was the triacet compound. Analysis of the substance melting at 304°–305°, dried at 100°:

0.1576 gram substance gave 0.2292 gram AgBr.

	Calculated for $C_{18}Br_8O_8(COCH_3)_2H_2$.	Found.
Br	61.54	61.87

Properties of the Diacet Compound.—It crystallizes in small prisms of a brownish- or yellowish-white color, which melt at 304°–305°. It is soluble in chloroform or carbonic disulphide; slightly soluble in cold benzene or acetone, soluble when hot; essentially insoluble in alcohol, ether, glacial acetic acid or ligroin. It is not acted on by the three strong acids or by sodic hydrate.

Analysis of the substance melting at 273°–275°, dried at 100°:

I. 0.1581 gram substance gave 0.2191 gram AgBr.

II. 0.1529 gram substance gave 0.2120 gram AgBr.

	Calculated for $C_{18}Br_8O_8(COCH_3)_2H$.	Found. I.	Found. II.
Br	59.15	58.95	59.00

Porter[1] analyzed the same substance and obtained 59.29 per cent of bromine.

This triacet compound melts constantly at 273°–275° and, in appearance and solubilities, resembles the diacet body.

These results were confirmed by some experiments on the action of benzoyl chloride with the reduction-product. The action of these substances gave a product which melted con-

[1] This Journal, 31, 106 (1904).

stantly at 250°–255° after purification, and further treatment with benzoyl chloride altered neither the melting-point nor the composition. It was dried at 100° for analysis. Analysis II. was made with a sample which had been treated a second time with benzoyl chloride.

I. 0.1650 gram substance gave 0.1922 gram AgBr.
II. 0.1618 gram substance gave 0.1880 gram AgBr.

	Calculated for $C_{18}Br_8O_8(C_8H_5CO)_4H$.	Found. I.	II.
Br	50.46	49.56	49.45

These results indicate that the substance is a slightly impure tribenzoyl compound, which is confirmed by the somewhat indefinite melting-point. Unfortunately, lack of time prevented us from preparing a pure specimen.

In one preparation a different substance, melting at 285°–287°, was obtained, but in too small quantity for analysis.

Oxidation of the Reduction-Product.

Our experiments on this subject were not brought to an end, owing to the departure of one of us from Cambridge, but we think them of sufficient interest for publication even in this unfinished state.

When 0.5 gram of the reduced α-substance were mixed with 5 cc. of glacial acetic acid and treated with 1 cc. of fuming nitric acid of sp. gr. 1.50, the brown color of the original substance immediately changed to red. After 2 or 3 minutes a large quantity of water was added, the mixture thoroughly stirred, the precipitate filtered out, washed free from acid and dried at 100° for analysis (I.). The yield was quantitative. The same product was obtained by warming the reduction-product on the steam-bath with ordinary strong nitric acid. This was also dried at 100° for analysis (II.):

I. 0.1625 gram substance gave 0.2575 gram AgBr.
II. 0.1631 gram substance gave 0.2588 gram AgBr.

	Calculated for $C_{18}Br_8O_8H_8$.	Found. I.	II.
Br	67.09	67.44	67.51

This red product melted at about 295°, but it was shown to

be a mixture by extracting it with boiling chloroform, when four successive extracts melted as follows:

I.	275°–280°
II.	275°–280°
III.	280°–285°
IV.	285°–287°

These extracts consisted of small, red prisms mixed with a few pale-yellow needles. The residue, which had melted throughout this extraction at 290°–293°, was then treated with boiling chloroform in a continuous extracter, when orange needles were obtained which did not melt below 310°. The red prisms could not be converted into the yellow needles by boiling for half an hour with chloroform, or by any other method we have found as yet. The quantities of these two bodies were not enough for purification and analysis, but the work will be repeated in the near future, on a larger scale, in this laboratory.

A curious phenomenon was observed when the crude reduction-product of the α-bodies was boiled with alcohol or benzene, as it was converted into a substance with a striking pale-lilac color. This change did not take place if the purified reduction-compound was used. We thought, therefore, that it was probably due to the zincic acetate left from the reduction, and upon boiling the pure reduction-product with alcohol and sodic acetate or zincic chloride we obtained, in each case, the same pale-lilac substance. It turned brown at about 200°, but did not melt below 310°; it was essentially insoluble in water or most of the organic solvents; only slightly soluble in toluene or nitrobenzene, even when boiling. Hydrochloric acid converted it into a brown product. Nitric acid turned it red. Acetic anhydride and sodic acetate dissolved it and the brown product formed melted at 270°–273°. Owing to the difficulty of purifying this substance, we were unable to get satisfactory analytical results in the time at our disposal and therefore postpone the discussion of its nature until a sufficient number of data have been collected.

Reductions of the tetrabrompyrocatechine and of the hexa-

bromorthoquinopyrocatechine ether with zinc and acetic acid were studied, in the hope that they might throw some light on the reduction of the α-compounds. The same product was obtained in each case, that is, hexabromdihydroxypyrocatechine ether more or less impure. The product from the ether gave, with alcohol, a purple substance similar in appearance to that described in the last paragraph, but we think it is a different body from a study of its other properties.

Experiments with the β-Compounds.

Five-tenths of a gram of the β-benzyl alcohol compound, $(C_6Br_4O_2)_2.C_7H_7OH$, mixed with 0.5 gram dry sodic acetate, was boiled for 15 minutes with 5 cc. of acetic anhydride and then the brownish solution was precipitated with water. The light-brown, flaky product was recrystallized from a mixture of 1 part of benzene and 3 of methyl alcohol, until it showed the constant melting-point 210°, when it was dried at 100° for analysis:

0.1591 gram substance gave 0.2373 gram AgBr.

	Calculated for $(C_6Br_4O_2)_2C_7H_7OCOCH_3$.	Found.
Br	64.13	63.46

Properties of the Acetbenzylalcohol Tetrabromorthoquinone.—It crystallizes from a mixture of benzene and methyl alcohol, or of chloroform and common alcohol in small, white needles. It melts at 210° and is freely soluble in ether, chloroform, benzene, acetone, or carbonic disulphide; nearly insoluble in alcohol, glacial acetic acid or ligroin when cold, moderately soluble when hot; essentially insoluble in water. The three strong acids have no perceptible action on it, and the same is true of sodic hydrate.

If the action of acetic anhydride on the β-benzyl alcohol body is continued for 6 hours a dark, charred mass was obtained, from which a mixture of benzene and methyl alcohol extracted a few brown needles melting, after one recrystallization, at 190°–195°.

Sulphuric acid of sp. gr. 1.44 did not affect the β-benzyl compound. It was decomposed by acid of sp. gr. 1.65, giving

a brown product, which did not melt below 300° and turned red when treated with nitric acid.

Aniline dissolved the β-benzyl compound when warmed with it, but after removing the aniline with dilute hydrochloric acid the unaltered β-compound was recovered, as shown by the melting-point, 213°–215°.

The β-benzyl compound was unaffected by 3 per cent sodium amalgam, or by tin and hydrochloric acid. The β-methyl compound was converted into a black product by tin and hydrochloric acid and was slowly dissolved (on standing 2 weeks) by zinc and acetic acid.

The β-benzyl compound was recovered unaltered after boiling for an hour and a half with 5 grams of potassic dichromate, 5 cc. of sulphuric acid and 10 cc. of water. It was completely decomposed when strong sulphuric acid was used instead of dilute. The β-methyl compound behaved in the same way with these mixtures. With boiling, fuming nitric acid its color changed at first from white to green and later it was entirely decomposed. It was not affected by boiling with common strong nitric acid.

CAMBRIDGE, MASS.,
May 26, 1905.

Contributions from the Chemical Laboratory of Harvard College.

ADDITION-COMPOUNDS OF QUINONES AND TERTIARY AMINES.[1]

BY C. LORING JACKSON AND LATHAM CLARKE.

We were led to the study of the action of dimethylaniline on quinones by an experiment with tetrabromorthobenzoquinone, $C_6Br_4O_2$, which formed part of the extended study of this body now in progress in this laboratory. The strongly colored, unstable product of this reaction seemed so interesting that we tried to obtain similar compounds from other quinones and found that the reaction was one of general application. So far as we have been able to find, the only addition-compounds of

[1] The work described in this paper formed part of a thesis presented to the Faculty of Arts and Sciences of Harvard University, for the degree of Doctor of Philosophy, by Latham Clarke.

amines and quinones, previously made, are those of various quinones with nitranilines discovered by Heberand[1] and Niemeyer,[2] but most of these contain 2 molecules of the amine to 1 of the quinone, whereas all of our compounds, which were analyzed, contained 1 molecule of each substance. There is some question, therefore, whether they belong to the same class.

The strong similarity in properties between the products from quinone and those obtained by the action of dimethylaniline on trinitrobenzene and related bodies led us to include these in our field of work, but after a preliminary paper[3] had been published we found, to our mortification, that we were intruding on an investigation reserved by Professor Sudborough[4] and have, consequently, confined our work after this to the compounds from quinones.

Dimethylaniline gave colored compounds with all the true quinones at our disposal. All of these were unstable, but we succeeded in isolating and analyzing the products from tetrabromorthobenzoquinone, $C_6Br_4O_2$, tetrachlorparabenzoquinone, $C_6Cl_4O_2$, trichlorparabenzoquinone, $C_6HCl_3O_2$, tetrabromparabenzoquinone, $C_6Br_4O_2$, and trichlortoluquinone, $CH_3C_6Cl_3O_2$, which were made up of 1 molecule of the quinone combined with 1 molecule of dimethylaniline. The compound with chloranil may be taken as an example. Its formula is

$$C_6Cl_4O_2C_6H_5N(CH_3)_2,$$

and it forms shining prisms of an intense indigo-blue color, which melt at 105°. The substance is so unstable that special precautions[5] must be taken to insure a good melting-point or analysis. When exposed to the air it loses dimethylaniline rapidly and after a day only the pure chloranil is left. This, however, is one of the more stable of these bodies, as many of them could not be obtained in crystals at all, but their formation was inferred from the very marked colors produced on mixing the components.

[1] Ber. d. chem. Ges., **15**, 1976 (1882).
[2] Ann. Chem. (Liebig), **228**, 322 (1885).
[3] Ber. d. chem. Ges., **37**, 176 (1904).
[4] J. Chem. Soc., **79**, 522 (1901); **83**, 1334 (1903).
[5] Given under chloranil in the experimental part.

Similar results were obtained with other amines belonging to several different classes, and analyses were obtained of the more important derivatives of dimethylparatoluidine, which also were made up of 1 molecule of each constituent. With the other amines the formation of a compound was inferred from the appearance of a color, but care was taken to distinguish between the colors caused by these unstable addition-compounds and those due to the formation of a stable coloring-matter.

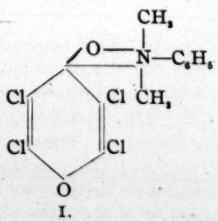
If these addition-compounds do not belong to the ill-defined class of molecular compounds, but their constituents are united to form a single molecule (which is not established), our experiments lead to the following, more or less probable, conclusions in regard to their structure:

The amines must be united to the quinones by the nitrogen, which thus becomes quinquivalent, because colors were obtained from dimethylaniline, monomethylaniline, parabromdimethylaniline, dibromdimethylaniline, dimethyltoluidines, dimethylnaphthylamines, diethylnaphthylamines, dimethylbenzylamine, dimethylisoamylamine, α-naphthylamine, tetramethyldiaminotriphenylmethane, diphenylamine and pyridine; and these substances have only one point in common, they all contain trivalent nitrogen and have, therefore, two affinities of the nitrogen free, ready for use in joining them to other bodies.

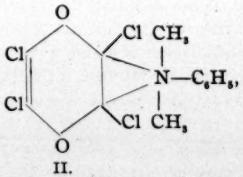
On the other hand, no colored compounds could be obtained from trimethylphenylium bromide, $C_6H_5N(CH_3)_3Br$, or iodide, and only traces of color were seen with the hydrobromide of dibromdimethylaniline, $C_6H_3Br_2N(CH_3)_2HBr$, just enough to be caused by a partial dissociation of the salt. The one fact observed by us, which is not in harmony with this conclusion, is the absence of color in experiments with tribenzylamine. This may be explained by the occupation of the space about the atom of nitrogen by the large benzyl molecules, which might prevent the action of its additional affinities, when the smaller methyl groups would have no such action, but much more experimental work is needed before this explanation can

be accepted with certainty and, in the meantime, the force of this objection to our conclusion must not be underestimated. We hope to undertake experiments in this direction in the near future.

The interpretation of our experiments is much more difficult, when we try to determine in what way the quinone is joined to the amine. That the formation of addition-compounds depends on the quinone structure seems to be established by the fact that colors were obtained from parabenzoquinone, $C_6H_4O_2$, and its derivatives (monochlorquinone, dichlorquinone, trichlorquinone, chloranil, bromanil, dibromquinone, dichlordimethoxy- or diethoxyquinone), from tetrabrom- or tetrachlororthobenzoquinone, from toluquinone and trichlortoluquinone, from dibromthymoquinone, from 1,4-naphthoquinone and from anthraquinone. On the other hand, no colors could be obtained from hydroquinones or pyrocatechins (tetrachlorhydroquinone, dichlordiisoamyloxyhydroquinone, dichlordibenzyloxyhydroquinone, or tetrabrompyrocatechine). The most probable ways in which the amine would be connected with the quinone would be either at the oxygen atoms or at the sides of the benzene ring; these two configurations are represented for the compound of chloranil and dimethylaniline by the following formulas,

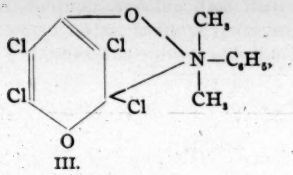


I.



II.

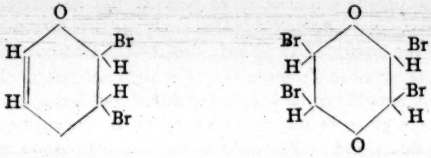
both of which look decidedly strange. The only other alternative would be that the addition took place partly on the ring and partly through the oxygen,



III.

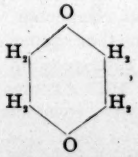
which seems even more improbable.

The experiments for determining which of these formulas is the most probable consisted (1) of those with compounds composed of saturated rings with atoms of oxygen in the quinone position, (2) of those with the oxygen atoms of the quinone modified. To the first class belonged our work with Nef's bromides of quinone.



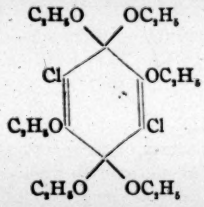
With the dibromide, colors were obtained with dimethylaniline; but the tetrabromide, in chloroform solution, gave at first no color and although, on standing, a coloration gradually appeared, we proved that this was accompanied by a splitting off of hydrobromic acid to form a substituted quinone.

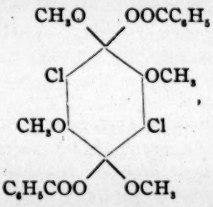
The paradiketohexamethylene,



also gave no reaction with dimethylaniline. It would seem, therefore, that an unsaturated ring is necessary for the formation of these addition-compounds.

Compounds with both quinone atoms of oxygen modified, such as dichlordiethoxyquinone tetraethylacetal and dichlordimethoxyquinone dibenzoyldimethylacetal,





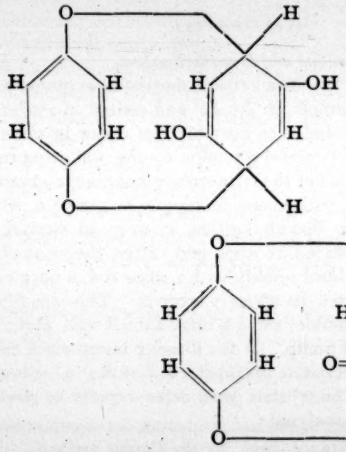
gave no colors whatever; and, while the quinone monoxime and dichlorquinone monoxime gave colors, no colors could be obtained from the corresponding dioximes.

These results would seem to point to the necessity of both an unsaturated ring and a quinone oxygen atom for the formation of the addition compounds—conditions which indicate the structure given in Formula III; but such an improbable constitution should not be adopted without convincing proof, and this is not given by our experiments, as is shown by the following discussion: The indifference of the dioximes might be explained by the reduction of the negative properties of the quinone, since it was found that the strongly negative derivatives of quinone formed more stable products than those which were more positive, for instance, the compounds obtained from trichlorquinone were found to be more stable than those from quinone in seven cases. It was observed, also, that the presence of large radicals attached to the quinone was unfavorable to the formation of our compounds. Thus dichlordiethoxyquinone, or dichlordimethoxyquinone, gave very unstable compounds, while the corresponding isoamyl and phenyl derivatives gave none at all. As, then, the dichlordimethoxyquinone barely forms these compounds, it is not surprising that the acetals mentioned above should refuse to act. These considerations weaken the force of the objections to Formula II. so much that it would not be wise to reject it.

On the other hand, the arguments against Formula I. are

but little weakened by a similar discussion, as the paradiketohexamethylene can hardly be so much more positive than quinone as to owe its indifference to this cause, and the presence of the bromine in the tetrabromide is not likely to prevent the formation of a compound, when bromanil forms a decidedly stable one.

We have left, therefore, Formula III., which is in harmony with all the observed facts, and Formula II., which can be brought into harmony with them with some little difficulty. Nevertheless, Formula II. may be more probable than III., as the latter represents an unusual form of addition, whereas II. suggests a relationship with quinhydrone, which Posner[1] has recently proved has one or the other of these formulas,



and our addition compounds show a most striking similarity to quinhydrone in composition and in their marked colors and instability.

Although, as already stated, trichlorquinone, owing to its

[1] Ann. Chem. (Liebig), 336, 90 (1904).

negative properties, gave more stable bodies than quinone itself, it was a curious observation that tetrachlorquinone, in four cases, seemed to give less stable products than trichlorquinone. Perhaps this may be due to steric effects. Trichlortoluquinone seemed to behave, in this respect, like trichlorquinone. Too much weight, however, must not be given to these observations, as they are somewhat indefinite.

It is, perhaps, worth mentioning that in the addition-compounds from dimethylaniline the presence of halogen in the quinone tends to impart a blue color to the substance; all those containing 2 or more atoms of halogen are blue or purple, those with 1 atom of halogen, or none at all, are red. The same rule applies to some, but not to all of the other amines studied.

EXPERIMENTAL.

Tetrabromorthoquinone and Dimethylaniline, $C_6Br_4O_2C_6H_5N(CH_3)_2$.—The tetrabromorthobenzoquinone was prepared by the method of Zincke[1] and melted at 150°–151°. The addition-compound is so unstable that it can be obtained, successfully, only by careful attention to the following conditions. One-half gram of the tetrabromorthoquinone, dissolved in 20 cc. of alcohol, was mixed, as rapidly as possible, with a solution of 0.5 gram dimethylaniline in 10 cc. of alcohol. A greenish color appeared at once and, after the sides of the beaker had been rubbed briskly with a glass rod, a purple precipitate was deposited in about 5 seconds. This was filtered off as quickly as possible, using a large funnel and perforated plate with the filter-pump. If the filtering lasted more than a few seconds the precipitate disappeared, forming a yellowish-brown solution. The crystals were dried rapidly by pressure on filter-paper and analyzed:

0.0528 gram substance gave, by the Carius method, 0.0720 gram AgBr.

	Calculated for $C_6Br_4O_2C_6H_5N(CH_3)_2$.	Found.
Br	58.68	57.98

[1] Ber. d. chem. Ges., 20, 1777 (1887).

The substance, therefore, contains 1 molecule of each constituent.

The addition-compound of tetrabromorthoquinone and dimethylaniline forms fine, glistening, purple needles, which are so unstable that they are converted into a black wax in 3–5 minutes at ordinary temperatures, but keep somewhat longer if artificially cooled. In contact with alcohol the substance is decomposed even more rapidly.

Tetrachlororthobenzoquinone gave a similar result with dimethylaniline, but as the addition-product seemed to be even less stable than the tetrabrom body, no attempt was made to study it. Tetrabrompyrocatechine did not react with dimethylaniline.

Chloranil and Dimethylaniline, $C_6Cl_4O_2C_6H_5N(CH_3)_2$.—The tetrachlorparabenzoquinone used in this work was first carefully freed from trichlorquinone. The chloranil was dissolved in a little dimethylaniline and to the strong solution thus obtained, four times its volume of alcohol were added after a few minutes. Beautiful, blue crystals of the product separated, usually at once, or occasionally after the lapse of a few minutes. A more dilute solution gave very handsome, large crystals after standing for some hours, but we preferred to prepare it from the more concentrated solutions for fear that the substance might be partly decomposed by long standing with the solvent. It was dried for analysis by rapid pressing on filter-paper.

0.1290 gram substance gave, by the Carius method, 0.2018 gram AgCl.

	Calculated for $C_6Cl_4O_2C_6H_5N(CH_3)_2$.	Found.
Cl	38.64	38.68

It crystallizes in slender, blunt-ended prisms of a dark, intense blue color with a bronze reflex. It melts at 105°. In taking the melting-points of these substances the specimen should be freshly prepared and kept moist with dimethylaniline until the moment of taking the melting-point; it is then dried on filter-paper as rapidly as possible and put at once into the melting-tube. With these precautions very constant re-

sults were obtained in spite of the great ease with which these compounds decompose. This body decomposes rapidly on exposure to the air, the dimethylaniline evaporating off. The decomposition begins as soon as the substance is exposed to the air, becomes very evident in the first half hour and after standing for less than a day all the dimethylaniline has evaporated and pure chloranil is left. When the crystals are covered with ether, chloroform, acetone, or ligroin the color changes in a few moments to green, or even yellow, from the extraction of the loosely combined dimethylaniline; alcohol gives a more stable, blue solution with it, especially if some dimethylaniline is present.

The mineral acids decolorize the crystals almost instantly with the formation of salts of the dimethylaniline. When heated to temperatures above its melting-point, the substance is converted into a dark blue product, undoubtedly identical with the coloring-matter described by Greiff,[1] patented by Meister Lucius and Brüning[2] and investigated by Wichelhaus.[3]

Trichlorparabenzoquinone and Dimethylaniline, $C_6HCl_3O_2C_6H_5N(CH_3)_2$.—This substance was obtained in just the same way as that from chloranil. It was dried rapidly on filter-paper and analyzed.

0.2037 gram substance gave, by the Carius method, 0.2535 gram AgCl.

	Calculated for $C_6HCl_3O_2C_6H_5N(CH_3)_2$.	Found.
Cl	32.03	30.76

It crystallizes in beautiful, slender prisms with blunt ends made up of four or more plates. It is dark blue with a bronze reflex and melts at 65°. It loses dimethylaniline on exposure to the air and is decolorized instantly by chloroform or the mineral acids. Alcohol decomposes the substance in a short time, unless it contains dimethylaniline, which renders the solution more stable. It dissolves without apparent decomposition in ether, benzene, or acetone.

[1] Ber. d. chem. Ges., 12, 1610 (1879).
[2] *Ibid.*, 13, 212, 2100 (1880).
[3] *Ibid.*, 14, 1952 (1881).

2,5-Dichlorparabenzoquinone and Dimethylaniline.—The dichlorquinone, prepared according to the method of Ling,[1] showed the melting-point 161°. It was dissolved in twice its weight of dimethylaniline, when a deep blue color appeared instantly, but the addition compound was not easy to obtain in the solid state. We finally accomplished this by allowing the solution in dimethylaniline to stand exposed to the air for several hours, when a network of very slender, deep blue needles was deposited. If the solution was allowed to stand too long another purple crystalline body separated, which was much more stable than the original addition-compound, as it dissolved unchanged in alcohol and even underwent boiling of this solution without any change of color. It is probably a coloring-matter similar to that obtained from the chloranil body. The addition-compound was rapidly decomposed, even in the cold, by all the solvents we have tried.

Chlorquinone, prepared by the method of Levy and Schultz,[2] gave, at once, a reddish-violet color with dimethylaniline and the addition of ether precipitated a dark red oil, which we have not succeeded in converting into a solid product. Quinone also gave a dark red color with dimethylaniline, but all our attempts to isolate a solid product failed. Alcohol gave a red oil; other solvents, as a rule, discharged the color. This color reaction can be obtained with very small amounts of either substance, so that it can be used as a test for a quinone or a dialkylamine.

Bromanil and Dimethylaniline, $C_6Br_4O_2C_6H_5N(CH_3)_2$.—The tetrabromparabenzoquinone was dissolved in a small quantity of dimethylaniline and, on standing, the addition-compound was deposited from the deep blue solution. It was dried for analysis by pressure with filter-paper.

0.4362 gram substance gave 0.6030 gram AgBr.

	Calculated for $C_6Br_4O_2C_6H_5N(CH_3)_2$.	Found.
Br	58.71	58.81

It forms a purple powder, which, under the microscope, ap-

[1] J. Chem. Soc., 61, 558 (1892).
[2] Ann. Chem. (Liebig), 210, 138 (1881).

pears as a network of fine, purple needles. It melts at 65°–68°; no sharper melting-point could be obtained. It is decomposed by solvents or the mineral acids.

Trichlortoluquinone and Dimethylaniline, $CH_3C_6Cl_3O_2C_6H_5N(CH_3)_2$.—Trichlortoluquinone, prepared according to Elbs and Brunschweiler,[1] gave a deep blue solution with dimethylaniline, which deposited, on standing, purple needles of the addition-compound.

0.1366 gram substance gave 0.1668 gram AgCl.

	Calculated for $CH_3C_6Cl_3O_2C_6H_5N(CH_3)_2$.	Found.
Cl	30.58	30.18

It is obtained by the spontaneous evaporation of its alcoholic solution in beautiful, flat, purple prisms, which melt at 68°–73° and dissolve, without apparent decomposition, in alcohol, benzene, or acetone.

Toluquinone, made by Clark's method,[2] gave a red solution with dimethylaniline, from which 90 per cent alcohol precipitated a red oil. Dibromthymoquinone gave a purple solution with dimethylaniline, from which dilute alcohol precipitated a purple oil that dissolved, with loss of color, in alcohol, ether, or benzene, but on evaporation of the solvent the color returned. Dichlordiethoxyquinone[3] also gave a reddish-purple color with dimethylaniline, but not even a colored oil could be obtained from the solution. Both 1,4-naphthoquinone[4] and anthraquinone gave a red color with dimethylaniline.

Bromides of Quinone and Dimethylaniline.

Nef's quinone dibromide,[5] $C_6H_4Br_2O_2$, gave, with dimethylaniline, a blue paste, from which we did not succeed in isolating a solid compound. It dissolved in alcohol, ether, or acetone without loss of color and is, therefore, decidedly stable for a substance of this class.

Quinone tetrabromide[6] gave a blue color at once with di-

[1] J. prakt. Chem., [2], **52**, 559 (1895).
[2] THIS JOURNAL, **14**, 555 (1892).
[3] *Ibid.*, **17**, 605 (1895).
[4] Made by the method of Japp and Miller. J. Chem. Soc., **39**, 220 (1881).
[5] J. prakt. Chem., [2], **42**, 182 (1890).
[6] *Ibid.*, [2], **42**, 182 (1890).

methylaniline, but, if the bromide was dissolved in chloroform, no color appeared until the mixture had stood for some time and the gradual formation of color after this was associated with the removal of hydrobromic acid, as proved by the following experiment:

Two-tenths of a gram of quinone tetrabromide were dissolved in 10 cc. of pure, dry chloroform and 0.2 gram of dimethylaniline added. The solution remained colorless and a test for hydrobromic acid gave a negative result. To make the test a small portion of the mixture was withdrawn, shaken with water and the aqueous extract treated with a drop of nitric acid and argentic nitrate. These tests were repeated at intervals of 5 minutes and gave negative results until the fourth time; then a slight trace of hydrobromic acid was detected and at the same time there appeared a faint blue color in the mixture. After another minute this color had become distinctly marked and a considerable amount of hydrobromic acid was present, while at the end of the fifth 5-minute period the color was very deep and the test for hydrobromic acid very strong. Such experiments have been repeated several times with the same result and it was found that the time of the appearance of the color and the test for hydrobromic acid did not differ more than 3 minutes in the several trials. With half the concentration of the solution of quinone tetrabromide the time before the appearance of the color and hydrobromic acid was longer, and, with double the concentration, it was reduced from about 20 to about 16 minutes.

The formation of hydrobromic acid, parallel with the appearance of the color, in all these experiments shows that the tetrabromide does not react with the dimethylaniline but that the addition-product is formed from the substituted quinone, produced by the removal of hydrobromic acid (as hydrobromide of dimethylaniline) from the quinone tetrabromide.

Oximes of Quinone.

Paraquinone monoxime, prepared by the method of Bridge,[1] was dissolved in alcohol and dimethylaniline added to the

[1] Ann. Chem. (Liebig), 277, 85 (1893).

clear, colorless solution ; a red color appeared at once, but no compound fit for analysis could be isolated. The addition-compound was evidently decidedly unstable, as the solution yielded a yellowish-green tar on standing. Quinone dioxime, made according to Nietzki and Guiterman,[1] gave no color with dimethylaniline. 2,5-Dichlorquinone monoxime, made according to Kehrmann,[2] gave a strong red color with dimethylaniline, but no compound was isolated, as the solution gave a yellowish-green tar on standing. On the other hand, no color was obtained when the 2,5-dichlorquinone dioxime[3] was mixed with dimethylaniline.

The following compounds gave no change of color when mixed with dimethylaniline :

Paradiketohexamethylene,[4]

$$C_6H_8O_2 ;$$

dichlordiethoxyquinone tetraethylacetal,[5]

$$C_6Cl_2(OC_2H_5)_2(OC_2H_5)_4 ;$$

dichlordimethoxyquinone dibenzoyldimethylacetal,[6]

$$C_6Cl_2(OCH_3)_2(OCOC_6H_5)_2(OCH_3)_2 ;$$

dichlordiisoamyloxyquinone,[7]

$$C_6Cl_2(OC_5H_{11})_2O_2 ;$$

dichlordiphenoxyquinone,[8]

$$C_6Cl_2(OC_6H_5)_2O_2 ;$$

dianilinobromquinoneanil,[9]

$$C_6HBr(C_6H_5NH)_2ONC_6H_5 ;$$

tetrachlorhydroquinone,

$$C_6Cl_4(OH)_2 ;$$

dichlordiisoamyloxyhydroquinone,[10]

$$C_6Cl_2(OC_5H_{11})_2(OH)_2 ;$$

[1] Ber. d. chem. Ges., **21**, 429 (1888).
[2] *Ibid.*, **21**, 3319.
[3] Obtained as a secondary product in making the monoxime.
[4] Hermann : Ann. Chem. (Liebig), **211**, 321 (1882).
[5] Jackson and Grindley : THIS JOURNAL, **17**, 633 (1895).
[6] *Ibid.*, **17**, 643 (1895).
[7] Jackson and Oenslager : *Ibid.*, **18**, 9 (1896).
[8] Jackson and Grindley : *Ibid.*, **17**, 595 (1895).
[9] Jackson and Porter : *Ibid.*, **30**, 531 (1903).
[10] Jackson and Oenslager : *Ibid.*, **18**, 10 (1896).

dichlordibenzyloxyhydroquinone,[1]

$$C_6Cl_2(OC_7H_7)_2(OH)_2.$$

Experiments with Derivatives of Dimethylaniline.

Parabromdimethylaniline[2] gave a red color with quinone, a blue color with trichlorquinone. Dibromdimethylaniline[3] gave a red color with quinone; with trichlorquinone a violet color. The hydrobromide of dibromdimethylaniline,

$$C_6H_3Br_2N(CH_3)_2HBr,$$

gave a slight red color after it had stood a few minutes with trichlorquinone, in alcoholic or benzene solution. The color was obviously due to a slight decomposition of the salt into hydrobromic acid and free dibromdimethylaniline. Trimethylphenylium bromide, $C_6H_5N(CH_3)_3Br$, or the iodide, gave no color reaction with either quinone or trichlorquinone.

Experiments with Dimethyltoluidines.

The dimethylparatoluidine and dimethylorthotoluidine were prepared by the method[4] contrived by one of us.

Chloranil and Dimethylparatoluidine, $C_6Cl_4O_2C_6(CH_3)H_4N(CH_3)_2$.—One and two-tenths grams of tetrachlorparabenzoquinone were dissolved in 0.8 gram of the dimethyltoluidine and the pale blue solution thus obtained allowed to stand until it deposited crystals of the addition-product, which were dried on filter-paper for analysis:

0.2881 gram substance gave 0.4338 gram AgCl.

	Calculated for $C_6Cl_4O_2C_6(CH_3)H_4N(CH_3)_2$.	Found.
Cl	37.10	37.22

It forms blue crystals, which give a violet powder and on standing in the air are converted into a green wax. It melts at 114° and is sparingly soluble in alcohol or acetone.

Trichlorquinone and Dimethylparatoluidine, $C_6HCl_3O_2C_6(CH_3)H_4N(CH_3)_2$.—A saturated solution of trichlor-

[1] Jackson and Oepslager: THIS JOURNAL, 18, 13 (1896).
[2] Weber: Ber. d. chem. Ges., 8, 715 (1875); 10, 763 (1877).
[3] Fries: *Ibid.*, 37, 2338 (1904).
[4] L. Clarke: THIS JOURNAL, 33, 496 (1905).

quinone in the dimethylparatoluidine, was allowed to stand for an hour and then mixed with its own volume of alcohol, when the addition-compound soon crystallized out. This body is very hard to obtain in a state of purity, because if the mixture stands too long before adding the alcohol it is converted into a black, sticky gum, and if, on the other hand, it does not stand long enough, the product is contaminated with unaltered trichlorquinone, which can be recognized by its yellow color. The pure compound was dried on filter-paper for analysis:

0.2171 gram substance gave 0.2719 gram AgCl.

	Calculated for $C_6HCl_3O_2C_6(CH_3)H_4N(CH_3)_2$.	Found.
Cl	30.58	30.96

It crystallizes in long, blue needles.

With dimethylparatoluidine, 2,5-dichlorquinone gave a deep blue color, monochlorquinone a light blue and quinone a brownish-red.

Trichlortoluquinone and Dimethylparatoluidine, $CH_3C_6Cl_3O_2C_6(CH_3)H_4N(CH_3)_2$.—The addition-compound was prepared by mixing its two constituents so as to make a concentrated solution, and adding to the deep blue liquid half its volume of alcohol. The substance crystallized out on standing and was dried on filter-paper for analysis:

0.2224 gram substance gave 0.2617 gram AgCl.

	Calculated for $CH_3C_6Cl_3O_2C_6(CH_3)H_4N(CH_3)_2$.	Found.
Cl	29.54	29.08

It crystallizes in fine, deep blue needles and melts at 74°–76°. It is decolorized by solvents almost instantly.

Bromanil and Dimethylparatoluidine, $C_6Br_4O_2C_6(CH_3)H_4N(CH_3)_2$.—The product crystallized out from a concentrated solution of the tetrabromparabenzoquinone in the dimethylparatoluidine, after it had stood for about half an hour. It was dried on filter-paper.

0.2312 gram substance gave 0.3092 gram AgBr.

	Calculated for $C_6Br_4O_2C_6(CH_3)H_4N(CH_3)_2$.	Found.
Br	57.14	56.93

It forms pale blue crystals, melting at 109°, which are essentially insoluble in alcohol, but are partially decomposed by it.

Dimethylorthotoluidine.—No definite compounds were isolated with dimethylorthotoluidine, but the following color reactions were obtained: With chloranil a red color was formed, which was discharged by solvents; the addition-compound is very unstable, since unchanged chloranil separated on cooling a hot solution of this body in the dimethylorthotoluidine. With trichlorquinone it gave a deep violet-red color which, apparently, was not discharged by ether, benzene, or acetone. The liquid was partially decolorized by alcohol, completely by acetic acid. No definite compound could be isolated. With tetrabromquinone the dimethylorthotoluidine gave a violet color; with quinone a brownish-red color; with toluquinone a bright red; with trichlortoluquinone a deep red color; with dibromthymoquinone a bright red; with 1,4-naphthoquinone a light red color.

Experiments with Benzylamines.

The dimethylbenzylamine used in this work was prepared by the method contrived by one of us.[1] Trichlorquinone, if treated with pure dimethylbenzylamine, was converted at once into a reddish tar, but if the quinone was dissolved in twenty times its weight of ethyl acetate, or toluene, and the amine added to the solution, a beautiful bright red color was produced instantly and on rubbing the sides of the beaker with a glass rod tufts of red, microscopic crystals were deposited. All our attempts to analyze this substance failed, as the crystals melted down to a green wax before they could be removed from the beaker or dried.

Quinone dissolved in ethyl acetate gave a deep red color on the addition of dimethylbenzylamine. On evaporating off the solvent a dark red oil was obtained, which could not be brought to solidification, although it dissolved in benzene, acetone, or ether without change of color. Tribenzylamine, made by Mason's process,[2] gave no color reaction with any of the quinones at our disposal.

[1] L. Clarke: THIS JOURNAL, 33, 496 (1905).
[2] J. Chem. Soc., 63, 1314 (1893).

Experiments with Dimethylisoamylamine.

The dimethylisoamylamine was made by the method contrived by one of us.[1] With trichlorquinone it gave a dark red color and, if the reaction took place in benzene solution and the sides of the beaker were rubbed with a glass rod, red crystals separated, which turned to a red wax in a few seconds, so that it was impossible to obtain an analysis or melting-point. Quinone gave a red color with the dimethylisoamylamine. If the reaction took place in benzene solution, a red oil was obtained by evaporation of the solvent, but it could not be brought into a state fit for analysis.

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Experiments with Naphthylamines.

Two-tenths of a gram of dimethyl-α-naphthylamine[2] and 0.2 gram of trichlorquinone were dissolved in 1 cc. of benzene and warmed on the water-bath. As the benzene slowly evaporated, a deep blue solution was obtained, from which the addition-compound was deposited in blue-black, lustrous crystals, after standing in the cold for from 1–2 hours. The substance was decolorized by solvents. It would have been easy to analyze this and several of the substances mentioned later, but, in view of the constancy of the results already obtained, it did not seem worth while to take the time for additional analyses.

Chloranil gave a blue oil, when dimethyl-α-naphthylamine was added to its solution in benzene. This did not solidify even in a mixture of ice and calcic chloride; it was not decolorized by the common solvents, but a few minutes on the water-bath converted it into a red oil, which gave a strong test for hydrochloric acid. Quinone gave a light red oil with dimethyl-α-naphthylamine; trichlortoluquinone a purple color.

Diethyl-α-naphthylamine[3] was added to a benzene solution of trichlorquinone and the mixture allowed to stand 10 minutes, when, upon evaporating off the benzene with a current of air, blue needles of the addition-compound were obtained, which became sticky if allowed to stand in the solution and, after

[1] L. Clarke: THIS JOURNAL, 33, 496 (1905).
[2] Made according to Friedländer and Welmans: Ber. d. chem. Ges., 21, 3124.
[3] Prepared according to Morgan. J. Chem. Soc., 77, 823.

several hours, were converted into a red tar. The diethyl-α-naphthylamine gave a dark red color with quinone, with trichlortoluquinone a dark blue, with 1,4-naphthoquinone a red.

Diethyl-β-naphthylamine[1] was added to trichlorquinone, dissolved in ether; as the ether evaporated, the addition-compound crystallized out in sharp needles, black by reflected, greenish by transmitted light. Bromanil, under similar conditions, gave black, lustrous prisms. Quinone gave a light purple color. Trichlortoluquinone, dissolved in benzene, was mixed with the amine and if, after warming for a few minutes on the water-bath, the benzene was allowed to evaporate, the product was a green oil, which deposited long, slender, blue-black needles, after it had stood a few minutes.

α-Naphthylamine mixed with a toluene solution of trichlorquinone, gave a bluish-green color, but no crystals could be obtained, as a brown wax was formed in about 10 minutes. With monochlorquinone, in toluene solution, a purple color was obtained, which soon turned brown; with quinone brownish-red needles, which seemed comparatively stable; with trichlortoluquinone deep blue crystals, also comparatively stable.

Experiments with Other Amines.

Diphenylamine gave, with either chloranil or trichlorquinone, black, very unstable crystals; with bromanil a deep blue color.

Pyridine gave a red color at once with chloranil and, after standing 10 minutes, brownish-red plates separated, which changed to a black wax in less than a minute.

Monomethylaniline gave a deep blue color with trichlorquinone or chloranil.

Tetramethyldiaminotriphenylmethane gave with quinone, in benzene solution, a violet color, and, on evaporating off the benzene slowly with a stream of air, flat prisms of a purple-violet color were obtained.

CAMBRIDGE, MASS.,
May 26, 1905.

[1] Morgan: J. Chem. Soc., 77, 823.

Contributions from the Chemical Laboratory of Harvard College.

THE ACTION OF METHYL ALCOHOL ON HEXABROMORTHOQUINOPYROCATECHIN ETHER.

By C. Loring Jackson and P. A. Shaffer.

After Porter and one of us[1] had found that methyl alcohol forms with tetrabromorthobenzoquinone three addition-compounds—$(C_6Br_4O_2)_2.CH_3OH$ in the α- and β-isomers and $(C_6Br_4O_2)_4.CH_3OH$[2]—it became of interest to see whether other orthoquinones behaved in the same way. We have, therefore, studied the action of methyl alcohol on hexabromorthoquinopyrocatechin ether, $C_6Br_4O_2C_6Br_2O_2$, which may be considered a tetrabromorthoquinone with 2 atoms of bromine replaced by the pyrocatechin residue, $C_6Br_4O_2$. Our experiments showed that when these bodies stood at ordinary temperatures a reaction did take place, but so slowly that even after 6 months not enough of the product had been formed for analysis and study. The presence of nitrobenzene as a solvent increased the yield, but still left much to be desired, so that we could hardly have determined the nature of this product if we had not found a method which gave it easily, with essentially a quantitative yield. This consisted in adding to the hexabrom ether, suspended in methyl alcohol, just enough sodic methylate to bring it into solution when, upon the addition of an acid, the product obtained showed itself, by its properties, identical with that made by the direct action of methyl alcohol. Its formula is $C_{13}Br_6O_4.(CH_3OH)_2$, so that it is formed by the addition of 2 molecules of methyl alcohol to 1 of the ether. It crystallizes in white, rhombic plates, which melt, with reddening, at 220°–221°. This decomposition by heat would indicate that it belongs to the α-series, but no addition-compound has been obtained from tetrabromorthoquinone with this proportion of methyl alcohol, so that, although related to the α-series, it does not strictly belong to it.

By determining the amount of sodic methylate necessary to make the compound we found that its sodium salt had this

[1] This Journal, 31, 89 (1904).

[2] Jackson and Carlton: *Ibid.*, 34, 422 (1905).

formula, $C_{12}Br_6O_4.CH_3OH.CH_3ONa$, and gave a neutral reaction with litmus. We could not find out whether it also gave another salt with twice as much sodium, as the sodium salts were so unstable that we did not obtain them in a state fit for analysis. The colored decomposition-products of the salt need further investigation.

Several other reactions of the hexabrom ether were studied in a preliminary way and yielded results which will be investigated in this laboratory.

Phenylhydrazine, diluted with nitrobenzene, reduced it to the hexabromdihydroxypyrocatechin ether,

$$C_6Br_4O_2C_6Br_2(OH)_2,$$

furnishing the most convenient method for preparing this substance yet discovered.

EXPERIMENTAL.

The hexabromorthoquinopyrocatechin ether,

$$C_6Br_4O_2C_6Br_2O_2,$$

was made by the method described by Koch and one of us,[1] in which we have introduced the following improvements: In making the tetrabrompyrocatechin, instead of recrystallizing the crude product (obtained from 20 grams of pyrocatechin) from 200 cc. of glacial acetic acid, it was washed first with about 100 cc. of this acid and then recrystallized from 75 cc. of it. The same portions of glacial acetic acid were employed repeatedly in different preparations, which led to a great economy in the amount of acid used, and increased the yield of tetrabrompyrocatechin without the trouble of working over the mother-liquors. After the crystallization the white product was washed with distilled water, which caused no darkening if, as usual, the product was pure; but if it was not, the dark impurities were precipitated from the adhering solution. The tetrabrompyrocatechin thus obtained melted between 186° and 187° and was, therefore, pure enough for our work. The yield varied from 78 to 80 per cent of the theory.

In oxidizing the tetrabrompyrocatechin to the orthoquinone,

[1] THIS JOURNAL, 26, 34 (1901).

much better yields were obtained if the acetic acid solution was cooled to about 12° before adding the nitric acid and the water added, after oxidation, was also cooled to 3°–4°. We found too (as observed by Carlton) that much more water should be used, the best amount for 15 grams of tetrabrompyrocatechin being 2 liters. With this cooling and dilution the quinone decomposed so slowly that no remarkable speed was necessary in filtering and washing it. It was found, however, that 15 grams was the largest amount that could be conveniently handled in this way and this gave 11–12 grams of tetrabromorthoquinone.

The yield of the hexabromorthoquinopyrocatechin ether[1] was about 75 per cent.

Action of Methyl Alcohol on Hexabromorthoquinopyrocatechin Ether.

In these experiments the ether was treated with methyl alcohol to see if it behaved like tetrabromorthoquinone. Two grams of the ether, mixed with 5 cc. of methyl alcohol, stood in a corked flask, at ordinary temperatures, for 6 months. At the end of this time it was found that a small quantity of a new substance had been formed, which crystallized in characteristic, rhombic plates. In the hope of hastening the action, 5 grams of the ether were boiled with 50 cc. of methyl alcohol, in a flask with a return condenser, for 2 days, but the filtrate from the unattacked ether yielded, after evaporation, a small, brown residue and none of the rhombic plates of the previous experiment. A better result was obtained when 5 grams of the ether, dissolved in 25 cc. of nitrobenzene and mixed with 50 cc. of methyl alcohol, were allowed to stand in a corked flask. After several weeks the rhombic plates began to appear and continued to be deposited for some months, but even this method did not give a satisfactory yield. Fortunately, a better method of preparing this substance was discovered in the action of sodic methylate on the ether, as described in the following section.

[1] THIS JOURNAL, **26**, 35 (1901).

Action of Sodic Methylate on Hexabromorthoquinopyrocatechin Ether.

Ten grams of the ether, suspended in 100 cc. of methyl alcohol, were brought into solution by the addition of just the right quantity of a solution of sodic methylate in methyl alcohol, containing 2 per cent of sodium. Hydrochloric acid or sulphuric acid was then added drop by drop, until the liquid had become slightly acid, which was shown by its change in color. After this the mixture was diluted with 200 cc. of methyl alcohol, heated to boiling for a few minutes on the steam-bath, filtered hot from the sodium salt precipitated and the filtrate cooled by immersion in ice-water for several hours, when the rhombic plates crystallized out. These were purified by washing with hot water till free from sodium salt and recrystallizing from hot alcohol, until they showed the constant melting-point 221°, when they were dried at 100° for analysis:

I. 0.4082 gram substance gave 0.3260 gram CO_2 and 0.0397 gram H_2O.

II. 0.4691 gram substance gave 0.3874 gram CO_2 and 0.0476 gram H_2O.

III. 0.2970 gram substance gave, by the Carius method, 0.4468 gram AgBr.

IV. 0.2559 gram substance gave 0.3845 gram AgBr.

	Calculated for $C_{12}Br_6O_4.(CH_3OH)_2$.	Found. I.	II.	III.	IV.
C	22.34	21.80	22.52		. .
H	1.06	1.08	1.12	. .	. .
Br	63.83	. .	. .	64.02	63.93

The substance is formed, therefore, by the addition of 2 molecules of methyl alcohol to 1 of the ether. The yield is essentially quantitative.

Properties of the Methyl Alcohol Hexabromorthoquinopyrocatechin Ether, $C_6Br_4O_2C_6Br_2O_2.(CH_3OH)_2$.—The substance crystallizes from alcohol in white, rhombic plates, which melt at 220°–221° with decomposition and evolution of gas. The compound begins to turn red at about 170°, if heated slowly. The products of this decomposition by heat are probably the

original ether and methyl alcohol. It is soluble in benzene or acetone; slightly soluble in alcohol or methyl alcohol; boiling alcohol dissolves about 4.3 per cent of it; insoluble in water. Strong hydrochloric acid did not seem to act on it, even when hot. A mixture of hot glacial acetic acid and fuming nitric acid dissolves it with a slightly red color, but on dilution with water the unaltered compound seems to be precipitated. Treatment with zinc and acetic acid apparently produced no change in it even after several weeks.

The substance forms a sodium salt. In fact this salt is the immediate product of the action of sodic methylate on the hexabrom ether. Several attempts were made to prepare this salt in a state of purity, but without success. As it is soluble in water as well as methyl alcohol, we tried to obtain it by evaporation, but, if this was carried on at low temperatures *in vacuo*, the residue turned dark green as soon as it became dry, and on treating such a residue with methyl alcohol a red solution was formed and a few of the rhombic crystals of the methyl alcohol compound were left. If the methyl alcohol solution of the salt was evaporated nearly to dryness, and water added at once, complete solution followed, but if it was allowed to stand a short time it turned green and then was only partially dissolved in water, giving a red solution, as described above. On boiling this solution with the insoluble residue, rhombic crystals of the free methyl alcohol compound were formed.

Although the salt could not be obtained in a state fit for analysis, we were able to determine its composition by a titration experiment. For this purpose a solution of sodic methylate in methyl alcohol was used, which contained 0.00416 gram of sodium in each cubic centimeter. This was added, from a burette, to 0.632 gram of the ether, suspended in 25 cc. of methyl alcohol and the flask containing the mixture was well shaken after each addition, when it was found that 5.1 cc. of the sodic methylate solution were needed to bring the ether into solution. These contain 0.0212 gram of sodium, whereas, if 1 atom of sodium had been used for each molecule of the ether, the amount would be 0.0211 gram. The solution thus

obtained was neutral to litmus and became alkaline on the addition of more of the sodic methylate solution. It is evident, from this experiment, that our new substance forms a salt,

$$C_{12}Br_6O_4.CH_3OH.CH_3ONa,$$

with a neutral reaction. We are unable to determine whether it also forms a salt containing 2 atoms of sodium.

The amount of bromine removed from the ether by sodic methylate did not rise above a mere trace, as 0.2 gram of the ether, mixed with methyl alcohol and sodic methylate, and then acidified with nitric acid and evaporated to dryness, gave, in the filtered solution of the residue, only a very slight turbidity with argentic nitrate.

Our work on the green decomposition-product of the salt was left unfinished from want of time, but some account of it may be given. If a neutral solution of the salt, formed by adding sodic methylate to the ether in the proportion of 1 molecule of each, was evaporated and the residue, after some time, dissolved in water, the red solution was found to have become acid to litmus paper, which we think was due to the liberation of a little of the methyl alcohol compound, $C_{12}Br_6O_4.(CH_3OH)_2$. The red color of this solution was due to a substance which was obtained in small amounts when the ether was treated with a large excess of sodic methylate, in methyl alcohol solution, and the product allowed to evaporate and stand over night. Upon adding very little water to the residue the new substance was left undissolved, in red needles. The following method gave what seemed to be the same product with a better yield :

The methyl alcohol compound, $C_{12}Br_6O_4.(CH_3OH)_2$, was boiled with a 20 per cent solution of sodic hydrate, when, on cooling, red needles appeared. The mixture was allowed to stand over night and then the crystals were filtered out on the pump and purified by crystallization from water, or better, as the substance was rather too soluble in water, a saturated aqueous solution of the product was treated with one-third to one-quarter of its volume of strong sulphuric acid, which precipitated the substance in light red needles. These, on recrys-

tallization from water, took on the darker red color of the preparations purified by crystallization alone. Unfortunately, in the time at our disposal, we could not prepare enough of this substance for analysis. It crystallizes in red needles, which do not melt, but at about 280° decompose with evolution of gas, leaving a black, charred mass. This decomposition-point seems to be nearly as well defined as a melting-point. The substance is soluble in both water and alcohol.

When the methyl alcohol compound was treated with methyl alcohol and bromine, a new substance was formed which melted, in the crude state, at about 150° without decomposition. This seemed to be different from the white product[1] of the action of bromine and methyl alcohol on the red hexabrom ether, as a sample of that melted at about 212°, with reddening and evolution of gas. What seemed to be still a third product was made by adding a little bromine to acetone and then treating the methyl alcohol compound with the colorless liquid.

Other Reactions of the Hexabromorthoquinopyrocatechin Ether.

Sodic ethylate, in ethyl alcohol solution, acted very slowly on the ether and gave a dark-colored product different from the methyl alcohol compound, but resembling in appearance that obtained by heating the ether with aqueous sodic hydrate. This last reagent had no perceptible action in the cold.

Bromine in ethyl alcohol, on the other hand, gave a white product after standing for several weeks with the red ether. No action was observed with benzyl alcohol or glacial acetic acid, even after standing for 7 months. Phenol gradually dissolved it, but on removing the phenol with water the unaltered ether was recovered.

Phenylhydrazine acted vigorously with the solid ether, forming a dark brown product, with evolution of white fumes. When the reaction was rendered less violent by the use of a solvent, a much purer product was obtained; we, therefore, found it best to proceed as follows: One part, by weight, of the ether was mixed with 5 parts of nitrobenzene and then

[1] This substance was made by Porter.

phenylhydrazine was added, drop by drop, shaking thoroughly after each addition, until the red color of the ether had been discharged. The nitrobenzene was then washed out with alcohol and the light brown residue was purified by recrystallization from boiling alcohol, when it appeared in long, white needles which mat together like asbestos. On standing for some days, in the light, the crystals turn brown. They show the solubilities of the hexabromdihydroxypyrocatechin ether, $C_6Br_4O_2C_6Br_2(OH)_2$, and it was proved to be this substance by a careful comparison of our product with one obtained by Dr. Russe in his work on the action of acetone on tetrabromorthoquinone. This reaction with phenylhydrazine is the easiest method yet found for preparing the hexabromdihydroxypyrocatechin ether.

The work on the substances mentioned in this paper will be continued in this laboratory.

CAMBRIDGE, MASS.,
June 12, 1905.

THE ATOMIC WEIGHT OF RADIUM AND THE PERIODIC SYSTEM.

BY HARRY C. JONES.

The question of the atomic weight of radium cannot be regarded, as yet, as settled. We have, on the one hand, the determination, by purely chemical means, made by Mme. Curie,[1] which gave the value 225. On the other, we have the work of Runge and Precht,[2] based on a physical method, which gave a much higher value—258.

It is difficult, at present, to decide between these two. The value based upon spectrum analysis (258) places radium in the periodic system *after* thorium and uranium. In terms of the relation between the mass of the atom and its radio-activity, this is the position which it should occupy. The greater the mass of the atom, the less its stability and, consequently, the greater its radio-activity.

Various lines of argument have been advanced in favor of

[1] Ann. Chim. Phys. [7], 30, 137 (1904).
[2] Phil. Mag. [6], 5, 476 (1903).

the value 225. Perhaps the most important of these is the argument based upon the position of radium in the periodic system. Radium is closely allied chemically to barium, and the value 225 for its atomic weight places it in the same *group* with barium, in *series twelve*.

This line of argument has had considerable weight, and has been used in favor of the smaller mass for the atom of radium.

The object of this paper is to point out that if the atomic weight of radium is slightly greater than 250, it would find a place in the periodic system quite in accord with all its chemical and physical properties. Indeed, the position which it would then occupy would be rather more satisfactory than that which it would take if its atomic weight were 225.

If the atomic weight of radium were 252 to 256 it would fall in Group II. of the periodic system, along with barium and its homologues, but in a new series—*series thirteen*.

That this is the case can be seen by a glance at Mendeléeff's table of the periodic system. If we compare the atomic weights of the elements in a given group and in any two succeeding series, we shall find for the elements with the higher atomic weights a difference in the atomic weights, in general, of from 25 to about 31 or 32 units.

Thus, the atomic weight of strontium is 87.6, that of cadmium 112.4—difference 24.8. The atomic weight of barium is 137.4, which differs from that of cadmium by 25 units.

Passing to Group III., the atomic weight of yttrium = 89, differs from that of indium = 115 by 26 units. Indium differs from lanthanum = 138.9 by 23.9 units, lanthanum differs from ytterbium = 173 by 34.1, and ytterbium differs from thallium = 204.1 by 31.1 units.

Turning to Group IV. similar relations manifest themselves. Zirconium, atomic weight 90.6, differs from tin, whose atomic weight is 119.0, by 28.4 units. Tin differs from cerium, whose atomic weight is 140.25, by 21.25 units. Cerium differs from lead, whose atomic weight is 206.9, by 66.65, but since cerium is in Series 9 and lead is in Series 11, and there is no member in this group in Series 10, we must divide the above difference by 2, which gives us a difference per series of 33.32. Lead

differs from thorium, whose atomic weight is 232.5, by 25.6 units.

In Group V. the following differences appear: Vanadium, with an atomic weight of 51.2, differs from arsenic, with an atomic weight of 75, by 23.8. Arsenic differs from niobium = 94, by 19 units. Niobium from antimony = 120.2 by 26.2 points. Antimony from tantalum = 183 by 62.8, but since one series is missing between these two, this difference must be halved = 31.4. Tantalum differs from bismuth = 208.5 by 25.5.

In Group VI. relations of the same kind appear. Chromium, whose atomic weight is 52.1, differs from selenium = 79.2 by 27.1 units. Selenium differs from molybdenum = 96 by 16.8 units. Molybdenum differs from tellurium = 127.6 by 31.6 points. Tellurium differs from tungsten = 184.0 by 56.4, but as one series is here missing this must be halved = 28.2. Tungsten differs from uranium = 238.5 by 54.5, and halving this, on account of the missing series, we have 27.2.

The above relations suffice to show that two successive members in any group of the periodic system usually differ, in their atomic weights, by a number that is close to from 25 to 28 and may reach 31 or 32, or even higher. This shows that an atomic weight slightly greater than 255, and which might be as high as 257 or 258, would place radium quite as satisfactorily in the periodic system as the lower value 225.

It might be objected that there is no other member of Series 13 known, and that it would be *creating a new series* just for one element—radium.

It is difficult to see the force of this argument in the light of the facts. In the first place, we know, at present, only two members of Series 12—thorium and uranium. Both of these are radioactive, but only feebly so.

While the placing of radium in Group II., Series 12, brings it in the same group with its chemical relative barium, it at the same time places it in a position which is not in keeping with its most characteristic physical properties. Think of radium as compared with thorium and uranium, or with any other chemical element. It is at least 1,500,000 times as

radioactive as uranium. It has the property of charging itself electrically, of lighting itself, and of giving off enormous quantities of heat energy. It is the only element known that has any of these properties to a determinable degree.

Further, it is very unstable, breaking down spontaneously and yielding another chemical element—helium—as one of its decomposition-products.

When we think of these properties alone it seems much more natural to place radium in a series by itself, following the series containing the slightly radioactive elements—thorium and uranium—than to place it in a series with any other chemical element or elements.

If we examine the evidence existing in favor of the value 225 we find, in the first place, the direct determination by Mme. Curie. It must be admitted that this is far from satisfactory, for a number of reasons. The small quantity of material at disposal made the result less accurate, assuming that the material was pure. A number of the operations to which it was subjected, such as removal of the water by heating in the air, are open to criticism.

Another argument in favor of the 225 value is based upon the fact, now pretty clearly established, that radium is a decomposition-product of uranium and must have a smaller atomic mass than the substance which produced it. This line of argument has been invalidated by the observation that *radium is certainly not formed directly from uranium*, but intermediate substances are produced and, as Joly[1] has pointed out, the radium probably results from the interaction of these products with some of the elements in pitchblende. Its atom could then easily have a mass greater than the atom of uranium itself, since radium would thus be a product of synthesis and not of decomposition. It must be stated that certain determinations by Watts[2] and others, using relations between the spectral lines, led also to a value close to 225. The meaning of this remains to be explained.

The direct argument in favor of the higher value is fur-

[1] Nature, 70, 80 (1904).
[2] Phil. Mag., [6], 6, July (1903).

nished by the beautiful investigation of Runge and Precht.[1] By means of certain relations between the spectral lines and the atomic weights of the elements producing them, which have been shown to hold for the members of a given group, as the magnesium, calcium, strontium, barium group, they were led to an atomic weight for radium of 257.8, or in round numbers 258.

As shown above, this would not move radium "two rows further down in the column Mg, Ca, Sr, Ba," as stated by Runge and Precht, and to which objections must be offered, but *only one row*, making it the only member of Series 13.

The atomic weight of radium can be settled, finally, only after a considerable amount of pure material is available. As some time must elapse before this is realized, the best we can do, at present, is to take the evidence available. The object of the present note, as has been stated, is to call attention to the fact that the argument based upon the periodic system, in favor of 225 as the atomic weight of radium, is not well founded. Indeed, the evidence from the periodic system is certainly as strong, and in the opinion of the writer much stronger, in favor of a higher value, which would be very nearly that found by Runge and Precht.

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PHENYLISOXAZOLONE.

BY ALFRED TINGLE.

In a recent article[2] Posner describes the preparation of phenylisoxazolone, $C_6H_5C{=}N.O.CO{-}CH_2$, from β-oxamino-β-phenylpropionic acid, $C_6H_5CH(NHOH)CH_2COOH$, previously[3] mistaken by him for α-oxamino-β-phenylpropionic acid,

$$C_6H_5CH_2CH(NHOH)COOH.$$

It seems desirable to call attention to the fact, which he ap-

[1] *Loc. cit.*
[2] Ber. d. chem. Ges., **38**, 2316 (1905).
[3] *Ibid.*, **36**, 4305 (1903).

pears to have overlooked, that the above phenylisoxazolone was first prepared by Claisen and Zedel,[1] by the action of hydroxylamine on ethyl benzoylacetate and by me, subsequently, from hydroxylamine and ethyl cinnamate, in the course of an investigation on "The Reactions of Aniline and Hydroxylamine with Hydroxy- and Unsaturated Compounds."[2] This work has had to be suspended on account of my removal from the United States. A knowledge of it would have saved Posner some labor and probably would have prevented his making the error into which he has fallen. I hope to resume my study of this subject later.

IMPERIAL PROVINCIAL COLLEGE,
CHINANFU, SHANTUNG, CHINA.
Sept. 10, 1905.

REVIEWS.

FOOD PRESERVATIVES, THEIR ADVANTAGES AND PROPER USE. The Practical versus the Theoretical Side of the Food Problem. By R. G. ECCLES, M.D., Pharm.D. With an Introduction by E. W. DUCKWALL, M.S. New York: D. Van Nostrand Company. 1905. pp. 202. Price, 50 Cents.

It is difficult to believe in the competency and sincerity of the writer of this book and therefore impossible to criticize it without writing a new volume. No examples need be given to justify the above opinion, as it is borne out on every page. The entire book is a tangled mixture of facts, misstatements and theories, which can hardly fail to mislead those unfamiliar with the subject. It is worthy of no further notice than is required to condemn it unreservedly. There is, of course, much to be said in favor of the judicious use of food preservatives and, when discreetly employed, they are undoubtedly a safeguard. Legislation controlling their use is, however, indispensable to prevent the more unscrupulous manufacturers from doing great harm. A. S. L.

AN INTRODUCTION TO CHEMICAL ANALYSIS FOR STUDENTS OF MEDICINE, PHARMACY AND DENTISTRY. By ELBERT W. ROCKWOOD, M.D., PH.D., Professor of Chemistry at the University of Iowa. Second revised edition. Philadelphia: P. Blakiston Son's & Co. 1904. Price, $1.50 net.

A review of the first edition of this useful manual appeared in 1902.[3] The publication of a second edition shows that it has gained the approval of instructors. E. R.

[1] Ber. d. chem. Ges., **24**, 140.
[2] THIS JOURNAL, **24**, 50 (1900).
[3] *Ibid.*, **27**, 235.

THE DETECTION OF POISONS AND STRONG DRUGS, Including the Quantitative Estimation of Medicinal Principles in Certain Crude Materials. By DR. WILHELM AUTENRIETH, Professor in the University of Freiberg. Authorized translation from the third German edition by WILLIAM H. WARREN, PH.D., Professor of Chemistry, Medical Department of Washington University, St. Louis, Mo. Philadelphia: P. Blakiston's Sons & Co. 1905. Price, $1.50 net.

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A translation of Professor Autenrieth's well-known manual is welcome and will prove very helpful to English-speaking students of chemistry, of medicine and of pharmacy. Professor Warren's translation is clear and well-worded.

Autenrieth's system is to classify poisons in four groups. Group I. comprises those volatile substances which may be distilled with steam, from an acid solution, without decomposition and includes yellow phosphorus, prussic and carbolic acids, chloroform, iodoform, aniline, nitrobenzene and carbon bisulphide. Group II. consists of non-volatile organic substances which do not distil with steam from acid solution, but may be extracted from impure mixtures by hot alcohol in the presence of tartaric acid; this group includes the alkaloids and many drugs, acetanilide, phenacetine, antipyrine, sulphonal, etc. Group III. includes the poisonous metals. In Group IV. we find acids, alkalies and a few poisons which do not fit into the preceding groups. Within the groups the individual poisons are detected by special reactions, chosen with excellent judgment.

The translator says in the introduction, "the brief comments of the author upon the fate, distribution and elimination of poisons in the animal body are a valuable feature of the last edition. The student learns what organs of the body should be examined for a poison in an actual analysis, what alterations it undergoes in metabolism and how it is eliminated. The introduction of the biological methods used in detecting arsenic and human blood add much to the completeness of the book." Frequent references to the literature of the subject increase the value of the work. E. R.

MANUAL OF CHEMICAL ANALYSIS, as Applied to the Assay of Fuels, Ores, Metals, Alloys, Salts and Other Mineral Products. By EUGENE PROST, D.Sc., of the University of Liège. Translated by J. CRUICKSHANK, B.Sc., F.C.S. London: Maclaren & Sons; New York: D. Van Nostrand Co. 1904. Price, $4.50 net.

This is a comprehensive but condensed manual; it is clear, the analytical methods are well chosen and it is a convenient work for the student.

The publishers could easily have printed it on thin, good paper, with decent type and have sold it at half the price de-

manded. The paper used is thick and coarse, the type worn and blurred, the drawings rude, the price ($4.50 net) out of proportion to the number of pages (300).

It is impossible to recommend this edition to students, they will do better to buy Rhead and Sexton's admirable manual,[1] which covers the same ground, but more completely, and is excellently printed and illustrated. E. R.

EINLEITUNG IN DIE CHEMISCHE ANALYSE. Erstes Heft. Kurze Anleitung zur Qualitativen Analyse, zum Gebrauche beim Unterricht in Chemischen Laboratorien. Bearbeitet von DR. LUDWIG MEDICUS, Professor an der Universität Würzburg. Zwölfte und dreizehte verbesserte und vermehrte Auflage. Tübingen: H. Laupp. 1905. Price, M. 2.

A review of the eleventh edition of Professor Medicus' valuable manual appeared in a former number.[2]

In this new edition one or two minor additions have been made, but, in the main, the book is unchanged. The dissociation theory is explained in the introduction, but is not utilized in the text. This book, it should be remembered, is the most popular manual in use in German laboratories and indicates a conservative spirit in Germany in the teaching of qualitative analysis. E. R.

A SHORT INTRODUCTION TO THE THEORY OF ELECTROLYTIC DISSOCIATION. By J. C. GREGORY, B.Sc. (Lond.), A.I.C. London, New York and Bombay: Longmans, Green & Co. 1905. pp. 76. Price, 50 cents.

This little booklet is just about what might reasonably be expected from the title. Even a casual glance brings out some peculiar English. On page 10 we read, "The digestion and incorporation within the general scientific system of new and apparently abnormal facts, must first be attempted by temporary attempts at explanation." On page 21, "Conductivity and resistance are reciprocals, and the less the latter is, the greater is the former."

On page 35, "It is evident that the more soluble a precipitate is, the greater does its solubility-product tend to be."

The reasons given on page 11, for assuming that molecules in solution are broken down into ions, are so inadequate as to leave an entirely wrong impression.

The book may prove helpful to those who cannot go more fully into the subject. H. C. J.

[1] Rhead and Sexton. "Assaying and Metallurgical Analysis." Longmans, Green & Co. 1902 (431 pages). Reviewed in this JOURNAL, 30, 82 (1903).
[2] THIS JOURNAL, 27, 235.